CSIRO PUBLISHING

*Aust. J. Chem.* **2018**, *71*, 953–956
https://doi.org/10.1071/CH18391

Full Paper

# $C_{60}$ as Electron Acceptor and Donor: A Comparative DFT Study of Li@$C_{60}$ and F@$C_{60}$

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Fullerene ($C_{60}$) is a stable prototype system for a special class of nanomaterials. In this work, the smallest alkali metal (Li) and halogen (F) atoms were encapsulated in the $C_{60}$ cage, and comparative quantum chemical calculations (QCCs) were performed on their various properties using a density functional theory approach. It was noted that the off-centre distance of Li is higher than that of F. The QCCs of the charge transfer to and from $C_{60}$ were also analysed. Although charge transfer to and from the $C_{60}$ cage takes place in both cases, Li@$C_{60}$ becomes more polar than F@$C_{60}$, suggesting a better electron-accepting nature of $C_{60}$ than electron-donating behaviour. This fact is consistent with the natural bond orbital (NBO) charge on the trapped atoms and the dipole moment as well as the binding energy values of the encapsulated $C_{60}$. Although the encapsulation of both atoms reduces the frontier orbital energy gap, the frontier orbital gap of Li@$C_{60}$ is smaller than that of F@$C_{60}$. More interestingly, the depression in the polarizability of Li@$C_{60}$ is significantly large relative to that of F@$C_{60}$. These findings also support the tendency of $C_{60}$ to act as electron acceptor. This study provides some insights into the fundamental properties of $C_{60}$ and should be helpful in designing new endofullerene complexes for a variety of applications.

Manuscript received: 6 August 2018.
Manuscript accepted: 1 October 2018.
Published online: 23 October 2018.

## Introduction

The most popular fullerene consists of 60 carbon atoms in the form of a hollow sphere, known as 'buckminsterfullerene' or a 'buckyball'. This was discovered by Smalley et al. in 1985;[1] however, the structure was identified a few years earlier by Iijima from an electron microscope image.[2] The hollow space enables fullerene to trap atoms or small molecules, and these were referred to as endohedral fullerenes or endofullerenes by Chai et al.[3] Heath et al.[4] discovered the first endohedral fullerene, La@$C_{60}$, by encapsulating an La atom inside $C_{60}$. Endohedral fullerenes have been interesting owing to their unique structures, novel electronic properties, and potential applications in a variety of fields, such as superconductors,[5] optical switches[6] solar cells,[7] and nanotechnology, and biomedical applications.[8] In the last few decades, many attempts have been made to dope $C_{60}$ using a variety of atoms and molecules[9–17] because of their electronic structures, which might exhibit different spin configurations. Endohedral fullerenes are also interesting because they serve as precursors to potential new materials for nanotechnology and semiconductors and, therefore, many theoretical and experimental studies have aimed to discover as well as synthesize these novel nanomaterials.[18–24]

Lithium (Li) and fluorine (F) are representative elements of the groups having the lowest ionization energy and highest electron affinity across the Periodic Table. Consequently, Li is more electropositive than C and F is more electronegative than C. Charge transfer takes places to and from $C_{60}$ when these atoms are trapped. Consequently, $C_{60}$ behaves as an electron acceptor in the case of Li@$C_{60}$ but an electron donor for F@$C_{60}$. The present work offers a comparative analysis of the various properties of Li@$C_{60}$ and F@$C_{60}$ using density functional theory (DFT). Many studies have been carried out on various aspects of Li@$C_{60}$[25–30] but only a few on F@$C_{60}$.[31,32] The objectives of the present study included whether $C_{60}$ is a better electron acceptor or electron donor. Further, we placed an emphasis on the changes in properties such as structural stability, and the vibrational and electronic properties of $C_{60}$ introduced by the trapping of Li and F atoms. We believe that this study provides better insights into the properties of endohedral fullerenes and should stimulate their possible applications.

## Computational Methods

In the present work, we used the B3LYP functional with the 6-31G(d) basis set as implemented in *Gaussian 09*.[33] B3LYP is

a three-parameter hybrid functional, which incorporates Becke's exchange term[34] mixed with the HF exchange and correlation term of Lee, Yang, and Parr.[35] The 6-31G(d) is a valence double-zeta polarized basis set in which six primitive Gaussian functions are used for core atomic orbitals, and valence orbitals are two basis functions comprising three and one primitive Gaussians. In addition, six *d*-type Cartesian–Gaussian polarization functions are included for each atom. The present computational scheme has already been found to be reliable in many previous studies on $C_{60}$ and related systems.[36–39] Geometry optimization was performed without any symmetry constraint in the potential energy surface. The vibrational frequency calculations were performed at the same level of theory. The atomic charges were calculated using a natural bonding orbital (NBO) scheme[40] as implemented in *Gaussian 09*.

## Results and Discussion

The equilibrium structures of $Li@C_{60}$ and $F@C_{60}$ are displayed in Fig. 1. The bond lengths of $Li@C_{60}$ and $F@C_{60}$ along with those of $C_{60}$ are listed in Table 1. We can see that the length of the C–C bonds in the hexagon–hexagon ($d_{H-H}$) rings as well as hexagon–pentagon ($d_{H-P}$) rings are slightly elongated by encapsulation of the Li or F atom. In the case of $Li@C_{60}$, the Li atom is located close to the pentagon side at a distance of 1.52 Å from the centre of the $C_{60}$.

Li and Tománek[27,28] already reported that the mean distance from the centre of Li inside $C_{60}$ was 1.5 Å, which agrees with the present calculations. In the case of $F@C_{60}$, the F atom is shifted and is 0.86 Å from the centre of $C_{60}$ cage. The equilibrium structures of $Li@C_{60}$ and $F@C_{60}$ were used to calculate their vibrational infrared spectra in the gas phase at the B3LYP/6-31G(d) level. For comparison, we also calculated the infrared spectrum of $C_{60}$ at the same level of theory. In order to assign the vibrational peaks, we analysed the graphical animation generated by the *Gaussview* program. Our vibrational analysis shows that all frequencies are positive for both $Li@C_{60}$ and $F@C_{60}$. This confirms that encapsulated $C_{60}$ belongs at the true minimum in the potential energy surface. We plotted the vibrational infrared spectra of $Li@C_{60}$ and $F@C_{60}$ along with $C_{60}$ in Fig. 2.

In $C_{60}$, we obtain four distinct peaks, two corresponding to two stretching (at 1460 and 1214 $cm^{-1}$) and bending (at 588 and 536 $cm^{-1}$) modes each. The encapsulation of the Li or F atom causes a modification in the intensity of the vibrational peaks due to change in the charge distribution and hence dipole moment. Note that the dipole moment of $C_{60}$ vanishes owing to its symmetry. However, $Li@C_{60}$ and $F@C_{60}$ possess non-zero dipole moments, 0.50 and 0.40 Debye (D) respectively (see Table 1), where 1 D is equal to the dipole moment of a pair of unit opposite charges situated at a distance of 0.208 Å. Therefore, vibrational peaks above 1500 $cm^{-1}$ are obtained in both $Li@C_{60}$ and $F@C_{60}$. The intense peaks observed at 1366 $cm^{-1}$ in $Li@C_{60}$ and 1222 $cm^{-1}$ in $F@C_{60}$ correspond to the bending of ring atoms in the cage. The infrared intensity distribution clearly shows that more intense peaks are seen in the $Li@C_{60}$ than the $F@C_{60}$ system. This indicates that the $Li@C_{60}$ cage becomes more polar than $F@C_{60}$, consistent with their dipole moment values.

In order to analyse the charge transfer in encapsulated $C_{60}$, we computed NBO charges on the trapped atom ($Q$), as listed in Table 1. One can see that the charges $Q$ on the Li and F atoms are +0.68 electron ($e$) and −0.40$e$ respectively. A charge transfer of 30% from the Li atom to the $C_{60}$ cage has been previously reported.[27,28] Although the first ionization energy of Li is quite low and electron affinity of F is fairly high, the $Q$ values are significantly smaller than unity. This may suggest the back-donation of charge within encapsulated $C_{60}$. For instance, there is back-donation of charge to Li from $C_{60}$ in $Li@C_{60}$ so as to reduce the net charge on Li to 0.68$e$. This was already noted in previous studies.[17,37] In the case of $F@C_{60}$, in contrast, there is significant back-donation from F to $C_{60}$ such that the C atoms

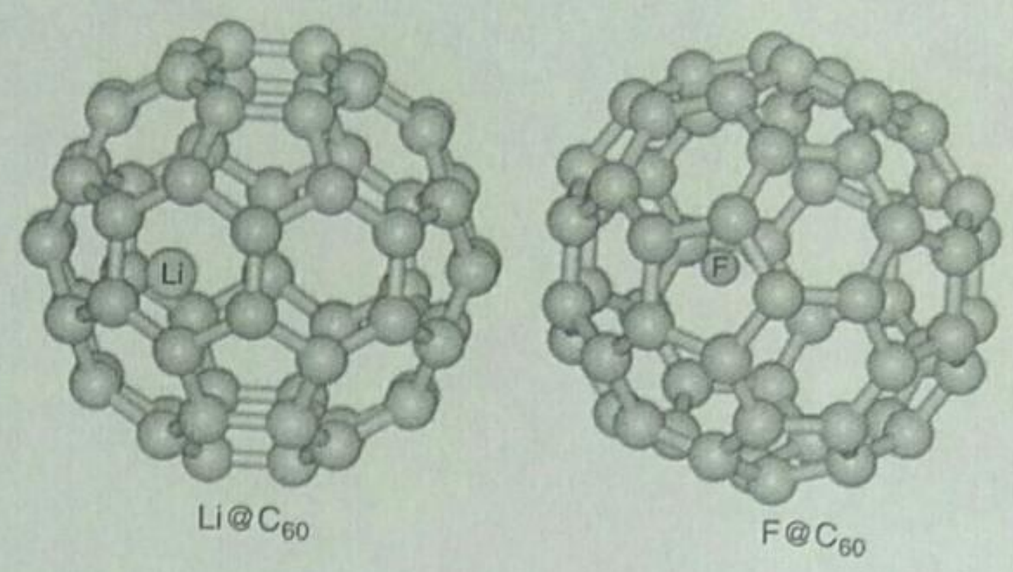


**Fig. 1.** Equilibrium structures of endohedral fullerenes considered in this study.

**Table 1. Various parameters of $Li@C_{60}$, $F@C_{60}$ and $C_{60}$ calculated at the B3LYP/6-31G(d) level**

| Parameters | | $Li@C_{60}$ | $F@C_{60}$ | $C_{60}$ |
|---|---|---|---|---|
| Bond lengths | $d_{H-H}$ [Å] | 1.40–1.41 | 1.40–1.41 | 1.40 |
| | $d_{H-P}$ [Å] | 1.45–1.46 | 1.45–1.46 | 1.45 |
| Distance from centre | $d_{centre}$ [Å] | 1.52 | 0.86 | |
| Binding energy per atom | $\Delta E$ [eV]$^A$ | 1.25 | 0.58 | |
| NBO charge on trapped atom | $Q$ [$e$] | 0.68 | −0.40 | |
| Frontier orbital energy gap | $E_{gap}$ [eV] | 0.88 | 1.08 | 2.76 |
| Dipole moment | $\mu$ [D] | 0.50 | 0.40 | 0 |
| Mean polarizability | $\alpha_o$ [au] | 501.0 | 477.4 | 468.8 |
| Depression in polarizability | $\Delta\alpha$ [au]$^B$ | −98.7 | −6.9 | |

$^A\Delta E = [60E\{C_{60}\} + E\{X\} - E\{X@C_{60}\}]/61$.
$^B\Delta\alpha = \alpha_o\{X@C_{60}\} - \alpha_o\{C_{60}\} - \alpha_o\{X\}$.

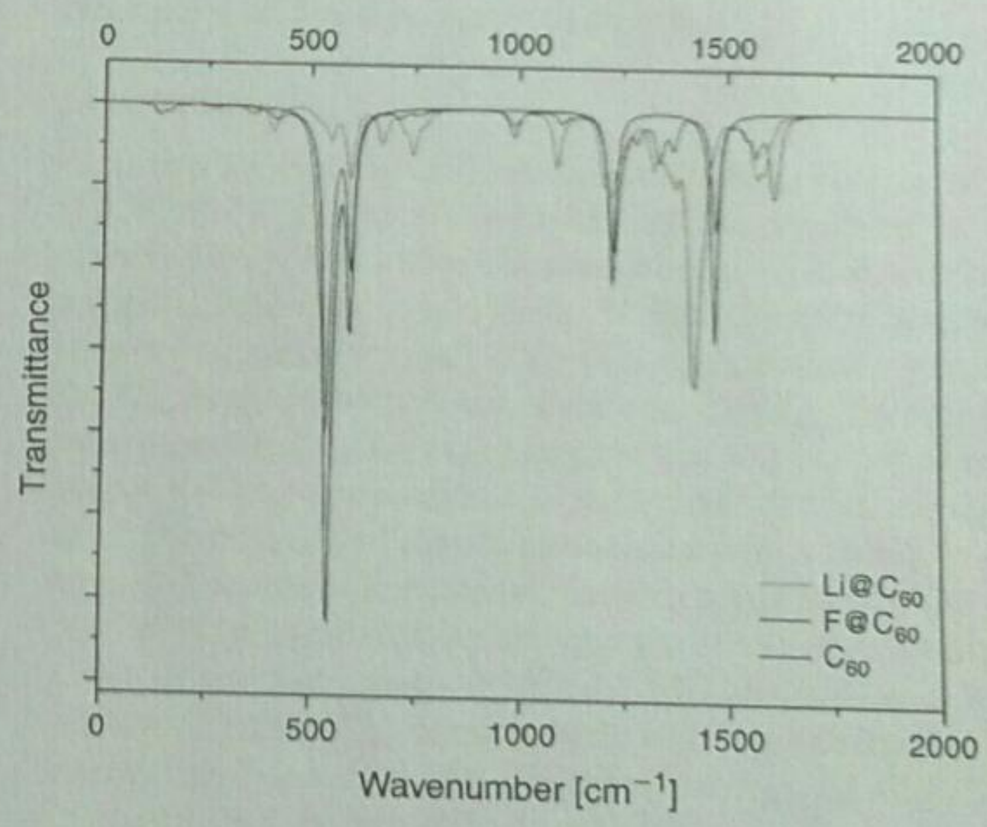


**Fig. 2.** Calculated vibrational infrared spectra of the systems considered in this study.

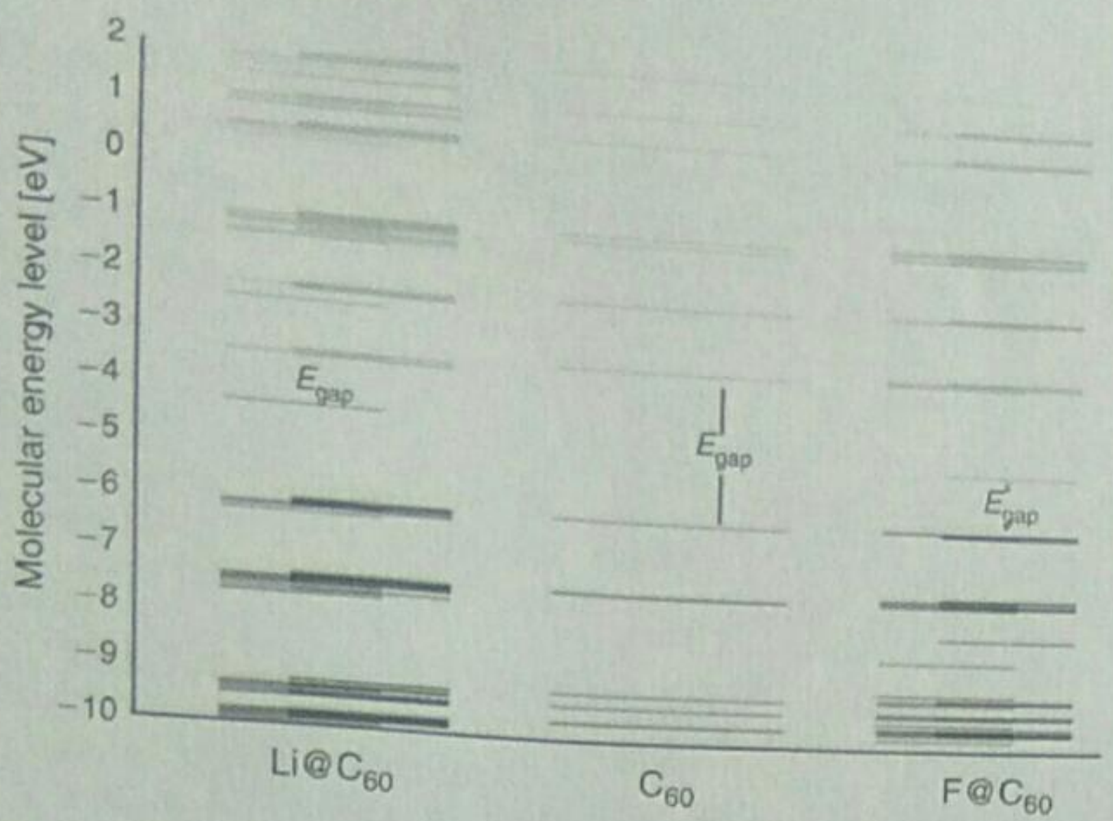


**Fig. 3.** Molecular orbital energy spectra of the systems considered in this study.

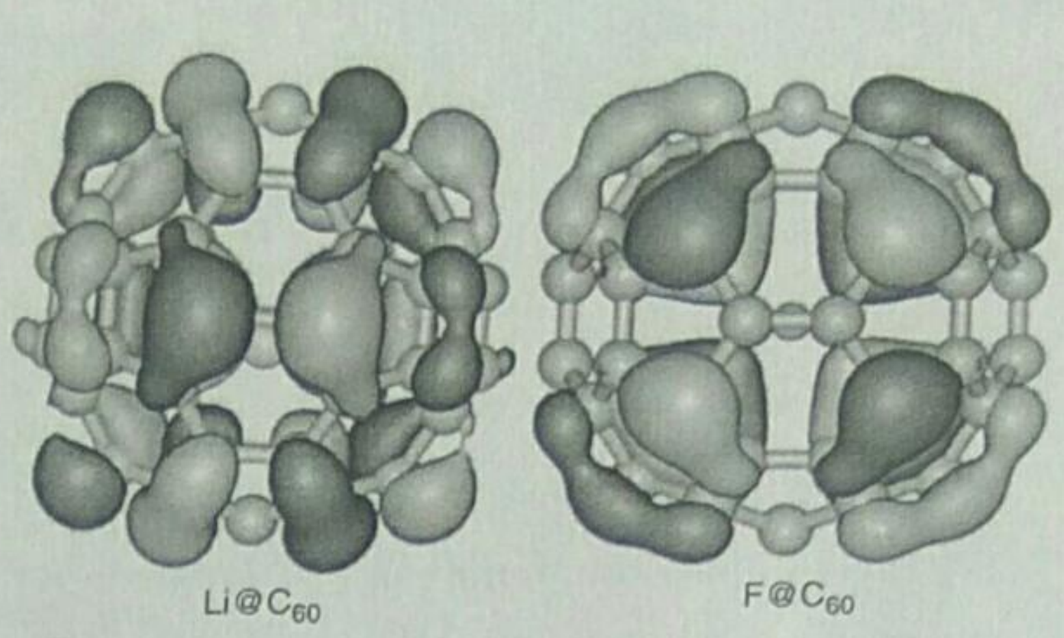


**Fig. 4.** The highest occupied molecular orbitals of endohedral fullerenes considered in this study.

become negatively charged (by $-0.003\ e$) in the vicinity of the F atom. On comparing the charge transfer to and from $C_{60}$ in both cases, we notice that $C_{60}$ is a better electron acceptor than electron donor. This is clearly reflected in the dipole moment values of Li@$C_{60}$ and F@$C_{60}$ mentioned earlier. Furthermore, this fact is supported by the binding energy per atom ($\Delta E$), listed in Table 1. Note that the $\Delta E$ of Li@$C_{60}$ (1.25 eV) is larger than that of F@$C_{60}$ (0.58 eV). This may suggest that $C_{60}$ becomes relatively more stable by accepting the charge from Li than by donating the charge to F.

The plotted molecular orbital energy level diagram of Li@$C_{60}$, F@$C_{60}$, and $C_{60}$ is shown in Fig. 3. The energy difference between frontier molecular orbitals such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is referred to as the frontier orbital energy gap ($E_{gap}$), marked in Fig. 3. One can see that the $E_{gap}$ value of $C_{60}$ is 2.76 eV, which decreases to 0.88 eV in Li@$C_{60}$ and 1.08 eV in F@$C_{60}$. This is possibly due to the fact that the encapsulation of Li or F introduces additional energy levels into the molecular orbital energy diagram. These additional energy levels tend to shift the HOMO energy up in Li@$C_{60}$ and the LUMO energy down in F@$C_{60}$, consequently reducing the energy gap. In Fig. 4, we show the HOMO surfaces of Li@$C_{60}$ and F@$C_{60}$. In both cases, the HOMO is contributed by C atoms of the cage. However, the major contribution comes from C atoms in the vicinity of Li in the case of Li@$C_{60}$ but C atoms far away in the case of F@$C_{60}$.

As encapsulated $C_{60}$ becomes polar owing to charge transfer to and from the Li or F atom, we calculated the mean polarizability ($\alpha_o$) of Li@$C_{60}$ and F@$C_{60}$, also listed in Table 1. The components of polarizability are computed by numerical differentiation using a uniform electric field of magnitude 0.001 atomic unit (au). The $\alpha_o$ of the empty $C_{60}$ cage, Li, and F atoms are 468.8 au ($\approx 70 \times 10^{-24}$ cm$^3$), 130.9 au ($19.37 \times 10^{-24}$ cm$^3$), and 1.67 au ($0.25 \times 10^{-24}$ cm$^3$) respectively, which agree well with the corresponding experimental values[41] of $76.5 \times 10^{-24}$, $24.33 \times 10^{-24}$, and $0.55 \times 10^{-24}$ cm$^3$ respectively. For encapsulated $C_{60}$, $\alpha_o$ increases compared with empty $C_{60}$ owing to charge transfer within the cage. In order to analyse the effect of the trapped atom on polarizability, we computed the depression in polarizability ($\Delta\alpha$). For Li@$C_{60}$, $\Delta\alpha < 0$, i.e. a depression of polarizability takes place (see Table 1). It has been already reported[42] that the encapsulated metal atom inside larger fullerenes such as $C_{60}$ is compressed and the total polarizability decreases. However, this depression is very small in the case of F@$C_{60}$ owing to the smaller magnitude of $\Delta\alpha$, 6.9 au relative to 98.7 au in Li@$C_{60}$. According to the model of quenched polarizability,[43] the polarizability of $C_{60}$ does not change significantly on encapsulation of atoms (molecules). Therefore, $\Delta\alpha$ is related to the decrease in polarizability of encapsulated atoms (molecules). Thus, the effect of encapsulation is stronger on Li atom than F atoms, as far as $C_{60}$ is concerned. This fact also agrees with the aforementioned properties of Li@$C_{60}$ and F@$C_{60}$. The theoretical results such the HOMO–LUMO energy gap, dipole moment, and polarizability discussed here may be useful in the design of charge-transfer complexes consisting of Li@$C_{60}$ and F@$C_{60}$ systems. Such complexes are likely to possess strong non-linear optical properties. Further work in this direction is in progress in our laboratory, and will be reported shortly.

## Conclusions

A comparative study on Li@$C_{60}$ and F@$C_{60}$ performed at the B3LYP/6-31G(d) level revealed that the structure of $C_{60}$ is equally affected by either encapsulation of Li or F, producing a marginal difference in bond lengths. The off-centre distance of F is, however, smaller than Li. There is charge transfer to and from the $C_{60}$ cage in both cases, although Li@$C_{60}$ becomes more polar than F@$C_{60}$. This may suggest that $C_{60}$ is a better electron acceptor than electron donor. This fact was further supported by the NBO charge and dipole moment as well as binding energy values. The molecular orbital analysis suggests that the encapsulation results in shifting the energy of the HOMO higher in Li@$C_{60}$ and the energy of the LUMO in F@$C_{60}$ is lowered relative to empty $C_{60}$, consequently reducing the frontier orbital energy gap, reducing the ionization energy of Li@$C_{60}$, and increasing the electron affinity of F@$C_{60}$. We also noted that the effect of encapsulation on polarizability is only marginal in the case of F@$C_{60}$ but that of Li@$C_{60}$ is strongly affected. These findings may be useful in the design of new systems based on these prototype endohedral fullerenes.

## Supplementary Material

The Cartesian coordinates of $C_{60}$ molecule and Li@$C_{60}$ and F@$C_{60}$ complexes are available on the Journal's website.

## Conflicts of Interest

The authors declare no conflicts of interest.

## Acknowledgements

The computational facilities provided by the Indian Institute of Technology, Kanpur, are acknowledged. Dr A. K. Srivastava also acknowledges the support of Professor S. N. Tiwari, Head of Department of Physics, DDU Gorakhpur University, Gorakhpur. This research did not receive any specific funding.

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UGC Approved Journal No – 47299
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# Climate Change and Traditional Method of Rain-Water Harvesting in Magadh Plain

*Dr. Kuntal Kishor*

*Climate change and its impact on geo-hydrological characteristics of land is a matter of concern for most of the world. Large numbers of projects and researches have been carried out by government and non-government organizations to find out the possible impact of climate change on availability of water. In view of changing geo-hydrological characteristics of lithosphere there is need of sustainable source of water. This study is aimed to find out the sustainability and reliability of traditional methods of rain water harvesting and use of harvested water for irrigation in Magadh region. Data and information collected from different secondary sources have been analyzed to find out the sustainability of these traditional methods. Since ancient times Ahar-Pyne system, Ponds and Tanks have been used in the study area for collection of rain and flood water and its distribution for irrigation purpose. Traditional methods of rain water harvesting have been found suitable for the study area as it is based on local geomorphic and climatic conditions. These methods are more sustainable and useful than modern methods of rain and flood water collection and distribution. Water harvested trough these methods can be used for irrigation purpose during dry season and during failure of monsoon. It also helps in recharging of underground aquifers.*

**Key Words** : Climate change, Geo-hydrological, Lithosphere, Sustainable, Rainwater harvesting, Ahar-Pyne, Monsoon, Aquifer.

**Introduction :** The human induced changes in climatic conditions have now gained a wide scale focus of the intellectuals and the governments all over the world. Environment scientists and Climate experts have not only warned us against the possible negative effects of climate change but also provided us the suggestions and the measures to be taken to get rid of it or to reduce its impact. It has now became a subject matter of almost all disciplines, such as: environmental science, environmental management, geography, earth science, urban and regional planning, meteorology, biogeography etc. One of the most disastrous effects of climate change is change in hydrological cycle and consequent changes in precipitation patterns and extremes of climate (cyclone, tornado). With the increase in population, industrial development and green revolution demand of water has increased voluminously for domestic, industrial and agricultural purposes. The ground water and surface water resources have been exploited without proper care and above the rate of replenishment. So, now pure water resource has become one of the scarce resources on earth. There is urgent need to replenish and conserve pure water for sustainable growth of human being. India lies in tropical belt and get most of her precipitation in the form of rainfall, so the rainwater need to be harvested as it flow down the slope towards the streams and drains, and ultimately reaches to the ocean without used. In higher latitude region precipitation is in the form of snow which does not flow quickly down the slope and thus, melt water slowly percolate to the underground aquifers.

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Climate change refers to the change in average weather conditions of any area that has been a characteristic feature of that area for a long period of time. The shift from average conditions of weather may be noticed by natural as well as anthropogenic causes. The last phase of natural climate change was witnessed during little ice age (14th century A.D.). The present discussion about the climate change is anthropogenic in nature. Industrial development and effluence of large scale pollutants, sizeable growth in population, decline in forest cover has resulted in increase in global average temperature due to green house effect and ozone depletion. It has further increased the concentration of carbon dioxide and Methane gas from thawing permafrost and warming ocean. Thus a cycle of increase in carbon dioxide concentration has begun. The chaos of global warming and disturbance in hydrological cycle has forced us to reconsider the sustainability of our present day water management techniques and to reintroduce the area based (ancient approach) of water harvesting based on long experience of local climatic and geo-hydrological conditions. This research paper tends to provide the assessment of ancient techniques used in Magadha plain for rain water harvesting and measures taken by the government and non-government organizations for its development.

Present study is focused on the methods adopted for water harvesting in Magadh plain since ancient times. The study area is situated in south-western part of Bihar. The plain is situated south of river Ganga, east of river Son, west of Anga plain and north of Peninsular plateau.

**Objective :** The main objective of the study is to assess the traditional method of rain water harvesting in the Magadh plain and its applicability in present circumstances. This study is also aimed to find out sustainability of these techniques in stipulation of changing precipitation pattern, failure of monsoon and geo-hydrological characteristics of study area. Researchers also tried to find out the historical development of these methods and social and technical conditions that assist its viability.

**Methodology :** Present study is based on analytical description of information gathered from different secondary sources. The study is historical in nature as it tends to explain the evolution and development of traditional water harvesting system, and it is idiographic in sense that it tends to provide the analytical description of the situation of water harvesting methods, sustainability of traditional method of rain and flood water harvesting and changing trend of water utilization habits.

**Geological Structure and Hydrological Characteristics of Magadha Plain :** The Magadha plain is surrounded by river Ganga in north, Son-Ganga divide in west, Anga plain in east and peninsular plateau in south. The predominant geological formations in Magadha plain are: mica schist, amphibolites, quartzite, granite dolerite and pegmatite of Proterozoic period, and gneisses, granite, phyllyte of Archean period ( in form of peninsular outgrowth) together with alluvial deposits of Ganga, Son, Falgu, Niranjana and its tributaries (Holocene period). The Vindhyan in Bihar are exposed in Rohtas and Bhabhua districts as scarp and plateau. The soils found in Magadha plain are: Sand, clay red and yellow, alluvial, and mixture of sorted gravels and sand, and of sand and clay.

The Magadha plain is drained by many rivers like Son, Falgu, Niranjana, Karmnasa, Durgawati, Dhamuti, Punpun, Morhar, Dardha, Paimar, Dhadhar, Sakri, Badua and Chandan. The average gradient of one meter per kilometer towards north and northeast in Magadha plain pushes the water from Rohtas and Chhotanagpur plateau towards river Ganga. This slope is the main driving force behind not only the major natural river system but also for canal and *Ahar-Pyne* irrigation system. The region gets average annual rainfall of 110 cm

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mainly during south west monsoon season. The failure of monsoon predicts the decrease in food crop production in the area, as most of the river and canal are rain fed and get less water during weaker monsoon.

The water bearing rock systems in the region are weathered and fractured granite rock and alluvium. The water bearing formation can be divided into-

a) Fissured formations- These are characterized by presence of fissure in rock strata or newly weathered parental rock. The ground Water is found in these fracture zones or in spaces between two rocks. The thickness of this formation is 2-10 meter in high ground and 10-15 meter in low lying area. The boreholes drilled by Central Ground Water Board (CGWB) in the hard rock terrain have tapped fractures at variable depth from 14-98 meter.

b) Porous formation- The Quaternary alluvium of river valleys constitutes this hydro geological unit. It consists of alluvial sediments made up of gravels, sands, silt and clays. The gravel and medium to coarse-grained sand layers are good groundwater repositories. The thickness of the alluvium deposit is nearly 30-50 meter.

**Water Utilization Habits and Sources of Water** : The whole population of Magadha plain depends on groundwater for their drinking need except few urban areas which get the water supply from nearby rivers. A part of the drinking need of towns in Magadh Plain is met from the Rivers due to lack of any potential aquifer beneath the towns. For agricultural and industrial use people depend on underground water, canal and other surface water reservoirs (Table-1).

Table-1

Total irrigated area through different sources in Magadh region

| Districts | Canal | Tube well | Other sources | Total irrigated area |
|---|---|---|---|---|
| Patna | 51115 | 121049 | 7431 | 179595 |
| Nalanda | 9442 | 164270 | 19576 | 193288 |
| Bhojpur | 40781 | 135775 | 11538 | 188094 |
| Buxar | 44421 | 66410 | 3079 | 113910 |
| Rohtas | 262570 | 36037 | 32227 | 330834 |
| Kaimur | 98493 | 54414 | 13630 | 166537 |
| Gaya | 232303 | - | 2787 | 235090 |
| Jehanabd | 596 | 57839 | 8771 | 67206 |
| Arwal | 28712 | 18034 | 1385 | 48131 |
| Nawada | 13944 | 108831 | 3783 | 126558 |
| Aurangabad | 142664 | 65794 | 15743 | 224201 |
| Total | 925041 (49.38% of total irrigated area) | 828453 (44.22% of total irrigated area) | 119950 (6.4% of total irrigated area) | 1873444 |

Source: Central Water Commission, Dept. of Water Resources, Bihar and Central Ground Water Board.

Farmers of Magadh region use pump set to fetch water from rivers and pond, and bore well to tap underground water for irrigation purpose. East and west Son canal is one of the main sources of irrigation in canal command area. For domestic use underground water is tapped through hand pump and bore well. Earlier, people used to depend on dug well to tap

groundwater for domestic purpose. For irrigation and industrial purpose people used to use Ahar- Pyne, Pond, River and Dug well. Potential sources of water in the region have been ground water, rivers and ponds.

**Traditional Methods of Rain Water Harvesting In Magadh Plain :** "In scientific terms, water harvesting refers to collection and storage of rainwater and also other activities aimed at harvesting surface and groundwater, prevention of losses through evaporation and seepage and all other hydrological studies and engineering inventions, aimed at conservation and efficient utilization of the limited water endowment of physiographic unit such as a watershed." The traditional methods of rain water harvesting that existed century ago in various states of India are relevant today as it is based on local conditions and are perhaps even more useful than the modern water harvesting techniques. These traditional methods of rain water harvesting were not only based on experience of local geo-hydrological conditions but also fitted to the long developed social mosaics. So, for the sustainable collection and utilization of rain water traditional methods are more useful than the modern one. *Ahar-Pyne, pokhar and well* are some traditional techniques used for rain water harvesting in the study area. Among these, *Ahar-Pyne* system is most successful and sustainable method of rain water harvesting and irrigation in Magadh region.

**Ahar and Pyne :** Agriculture practices developed in Magadh plain about 4000 years ago. *Ahar-Pyne* system was developed by the local farmers to have perennial access to water for irrigation. When, sufficient amount of water is not provided the productivity of crop decreases. During rainy season the area get 110 cm of rainfall and water from over flooding river and top rocky region flow down the slope. *Pyne*, a narrow man made channels running down the slope from base of a hill, river or pond collect over flowing water and ultimately ends in to an *Ahar* (a reservoir having embankment on three sides) [Figure-1]

Table-2 : Area irrigated by Ahar and Pyne system

| year | Area irrigated (mha) | Region covered |
|---|---|---|
| 1930 | 0.94 | South Bihar |
| 1971 | 0.64 | South Bihar |
| 1976 | 0.55 | South Bihar |
| 1997 | 0.53 | Whole of Bihar |

Source: http://www.indiana.edu/~iasep/Final paut.pdf.

Large network of *Ahar* and *Pyne* were developed during Mauryan and Nanda period and since then it has been used for rain and flood water harvesting. It was this irrigation system that allowed the farmer of Nalanda to feed more than 10000 students and 1000 teachers of ancient Nalanda University. Rivers like Punpun, Sone, Ganga, Morhar, Lilajan, Mohane, Phalgu, Dhadhar, Mangura, Jakori, Tilaiya, Khuri, Dhanarji, Sakari, Nata, Baghel, niranjana etc. supported this system of water harvesting. It loosed its importance partially due to development of modern canal irrigation system, tube well and bore well, pump set and mainly due to disorganization of social institutions set up for construction and maintenance of *Ahar* and *Pyne*. Since the introduction of new irrigation techniques by British and its continuous development during post-independence phase this method of rainwater harvesting losing its importance (Table-2). Some NGOs like DHAN foundation, Satyapath and Magadh Jal Jamaat have shown keen interest in rejuvenation of this system of rain water harvesting during recent past.

Figure 1
Ahar-Pyne system

Source: rainwaterharvesting.org

**Sustainability of *ahar-pyne* system :** In view of uncertainty of monsoon and change in climatic conditions it has been advised by the scholars that there is need of sustainable development of agriculture to feed our rapidly growing population. Sustainable development of agriculture demands for sustainable source of irrigation. Modern developed techniques such as tube well, bore well deplete the underground water and water table is gradually going down year by year. Further canals are not a perennial source of water in Magadh region. On the other hand ahar-pyne is best suitable method for rain water harvesting, recharge of underground aquifers and irrigation. In this region slope of ground is favorable for development of ahar-pyne which collect rain and flood water for irrigation. Some part of water collected in ahar percolate down the ground and recharge aquifers and rest are used for irrigation in dry season or during failure of monsoon. So it is sustainable and most suitable method of rain water harvesting in the study area developed by local farmers on the basis of their long experience of local geomorphic and climatic conditions.

**Other Methods :** Flood and rainwater move down the slope and collected in manmade or natural depression, we name it pond, tank or lake. The water harvested in ponds and tanks have been used by local farmers since ancient times. There were large number of tanks (in hilly region) and ponds (in plain) in the study area. But negligence and unavailability of proper maintenance of these reservoir most of them became plain and dry due to siltation. Some remaining ponds are still used by farmers for irrigation purpose. There is large pressure of population on these water bodies and they cannot meet the needs of local farmers. If these ponds and tanks are rejuvenated it can hold water for dry season and underground aquifers will also be recharged.

**Conclusion :** Recent changes in precipitation pattern due to climate change, drying surface water sources and depleting underground water due to non-replenishable excessive use of these water sources are some serious concerns for farmers, scholars and the governing bodies

in the study area. There is an urgent need to make efforts to provide sustainable source of irrigation to farmers and to recharge underground aquifers for growth of flora and fauna. Problem of water shortage in the region can be sorted out by rejuvenation of ahar and pyne system, ponds and tanks. These surface water sources are not only the back up for water needs during dry season but also help in recharging underground aquifers. Further, these water sources were developed by local farmers in accordance with the local climatic and geomorphic characteristics. So these are sustainable and reliable sources of water which needs less investment than development of canals and dams.

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Iran. J. Chem. Chem. Eng.

Research Article

UGC Approved Journal No : 49207

(IIJIF) Impact Factor : 3.712

Regd. No. : 1687-2006-2007

ISSN 2231-4113

# Śodha Pravāha

(A Multidisciplinary Peer Reviewed Refereed Research Journal)



VOL. VIII

ISSUE 3

APRIL 2018



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# Geography of Crime against Women in Metropolitan India

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*Spatial variation in rate of crime against women predicts the spatial pattern of women empowerment and social heath in different geographical area. This study tries to find out the spatial variation in crime against women in metropolitan cities of India having population above two million. It also incorporates the possible cause of this spatial variation. To know the spatial variation in crime against women, data and information has been collected from National Crime Record Bureau (NCRB) report of 2016, newspapers and journals. Data collected from secondary sources after statistical and descriptive analysis reveals the spatial variation in rate of different crimes against women. This study incorporates statistical, descriptive, comparative and analytical study of data related to crime against women in metropolitan cities of India which suggests that: Metro cities in north India register highest rate of crime against women followed by metro cities of central and south India, some crimes are more common in particular area. The possible causes for this spatial variation have also been briefly discussed in this paper. Therefore this study is an attempt to know the spatial variation in rate of crimes committed to women and the possible cause behind it.*

**Key Words:** Spatial variation, Spatial pattern, Women empowerment, Social heath, Statistical, Descriptive, Comparative, Analytical

**Introduction :** Crime against women in India is one of the least studied common phenomena. Since the advent of great human civilizations women played an important role in the development of society. Gifted with motherhood they nurtured the mankind to their optimum level of development but unfortunately crime against women has been the part of society since the beginning. Women in ancient India enjoyed respectable place in their societies but today women are easy prey for criminals and even family members. Male dominated social, economic, legal and political order (Atray 1998; Verma 1990; Nagia 1993 and Mukherjee 2001), activities for political gains (Karat, 1998), increasing participation of women in socio-economic, administrative and political system (Rajan 1981; Deshpande 1984 and Ganguli 1990) make women vulnerable to crime. In year 2016, 29 lakh FIRs were registered in India. Crimes against women contribute to about 10% of all crimes (Economic Times, Nov. 24, 2018). The recorded data of crime against women do not represent the actual number of incidents of crime against women in India. National Family Health Survey (2016) shows that less than 0.1% women who were victim of sexual violence went to the police. Crime victimization survey to know dark figure (Biderman, 1991) conducted in Rajasthan shows that only 29% of victims go to the police station and only 19% victims register case (Banerjee, Chattopadhyay, Duflo, Kensiton and Singh, 2012). So change in recent data regarding number of crime against women may be due to the change in reporting of crime. The rate of reporting of crime against women in metropolitan India is relatively higher than in rural areas. National Crime Record Bureau is a nodal agency that prepares report of different types of crimes including crimes against women in India on the basis of FIRs and complaints

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in different police stations. Total 11,761 cases of crime against women registered in Metropolitan cities (having population more than 2 million) of India in 2016. It is 5.16% of total crime committed in these Metropolitan cities (**Crime in India 2016 statistics, NCRB, Ministry of Home Affairs**). Low percentage of crime against women is only due to reasons associated with social stigma, malfunctioning of legal system and fear of retaliation (**Mukherjee, Rustagi and Krishnaji, 2001**). If proper reporting were done it would have increased up to 50% in Metropolitan India.

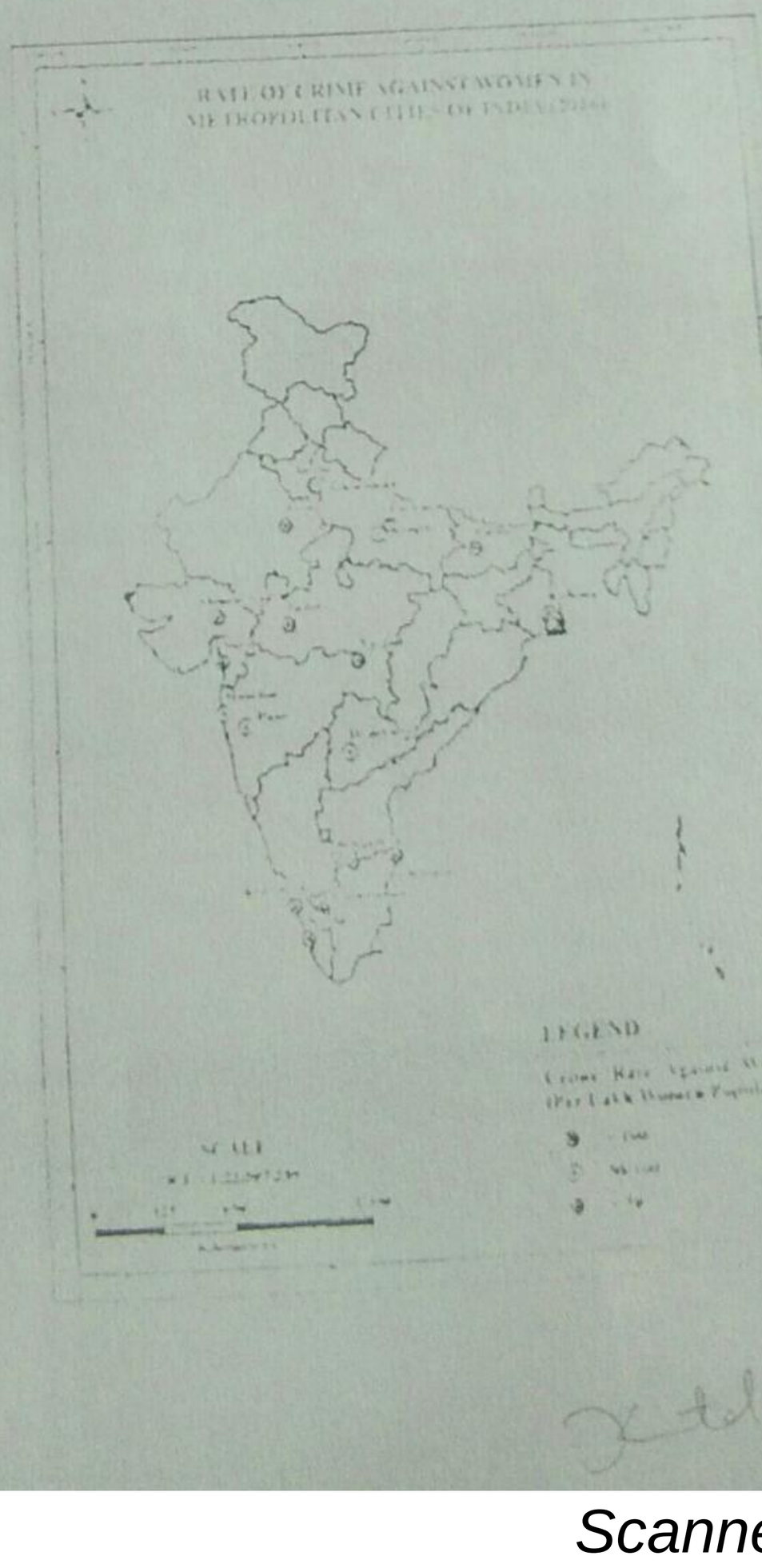
**Objective and methodology** : The main objective of this paper is to find out the spatial pattern of crime against women in metropolitan cities of India. For this purpose data has been collected from National Crime Record Bureau report (2016). These data has been analyzed to find out the spatial pattern, if any, of crime against women in big cities of India. Spatial pattern of intensity of different crimes against women have been calculated on the basis of averaged rank score of metro cities of north, central and south India. Averaged rank score for different crimes has been calculated by average of ranks of concerned towns in different parts of India (north, central and south). The city with highest crime rate has been given rank one and so on. Cities with same crime rate have been given same rank. The crime rate in this paper has been calculated as number of crime against women per one lakh women population. Region with low averaged rank score has highest intensity of crime and region with high averaged rank score has low intensity of crime. In this paper author has used descriptive, comparative and analytical approach to describe crime against women, its spatial pattern and spatial variation in metropolitan India.

**Crime against women in India: statistical overview** : In 2016 out of total 4831515 numbers of crimes reported in India 338954 crimes were committed to women. So, only 7% of reported crimes in India were committed against women. Rate of crime against women in India is only 55.2 (per lakh of women) which is 379.3 (per lakh population) for whole population of India (**NCRB report 2016**). The reported data of crimes shows that crime rate against women is significantly lower than the overall crime rate in India. But the actual picture is different from the statistical facts due to dark figure (**Biderman, 1991**). Rate of crime against women in twenty nine states of India is only 53.6. It is 137.6 for seven union territories of India.

**Crime against women in metropolitan cities of India: statistical overview** : Metropolitan cities have population above one million. There are 53 million cities in India (Census, 2011). Out of which 19 cities have population above 2 million. Metro cities with 2 million population are area of study in this research paper. It include, Delhi, Ghaziabad, Jaipur, Kanpur, Kolkata, Lucknow and Patna from northern India, Ahmedabad, Indore, Nagpur and Surat from central India, and Bengaluru, Chennai, Coimbatore, Hyderabad, Kochi, Kozhikode, Mumbai and Pune from southern India. Out of these nineteen metropolitan cities, Maharashtra and Uttarpradesh occupy three cities, Gujarat, Tamilnadu and Kerala occupy two cities, and Karnataka, Telangana, Madhyapradesh, Rajasthan, West Bengal, Bihar and union territory of Delhi occupy one city.

Average crime rate in cities having population above two million is 709.1. Highest crime rate among these nineteen cities has been found in Kochi (2553.1) followed by Nagpur (1714.6), Chennai (1308.6), Delhi (1263.9) and Surat (1243.3). Other metropolitan cities have crime rate less than 1000 per lakh population. Average rate of crime against women in the study area has been found 77.2. Highest rate of crime against women has been found in Delhi (182.1) followed by Lucknow (159.8), Jaipur (144.1), Patna (133.8), Nagpur (113) and Indore (101.4). In other thirteen metro cities rate of crime against women is below 100 per lakh

women population. Rate of crime against women is lowest for Coimbatore (9.5) followed by Chennai (12.6), Kolkata (24.9) and Surat (28.7). If we calculate averaged rank score for metropolitan cities in northern, central and southern India on the basis of crime rate (Table-1) we find that metro cities in central India have highest intensity of crime followed by metro cities of northern and southern India respectively. Average rank score for crime in Northern India = Sum of rank (on the basis of crime rate) of cities in Northern India ÷ Total number of metro cities in Northern India. So averaged rank score for metro cities in northern India = (4+12+6+17+19+10+8) ÷ 7 = 10.86. Similarly it is 10.63 for metro cities in Southern India and 7.25 for metro cities in Central India. Lower averaged rank score for crime in Central Indian metro cities means, high intensity of crime in these cities. Spatial pattern of rate of crime against women is different from the pattern for overall crime rate. Averaged rank score for rate of crime against women in north Indian metro cities is 6.286. It is 10 for central Indian metro cities and 13.25 for metro cities of southern India. On the basis of this we can conclude that as we move northward in India intensity of crime against women in metro cities increases. Out of total crimes in nineteen metropolitan cities concerned for this study, only 5.16% crime is committed against women. In Hyderabad 13.22% of total crime is committed to women. It is followed by Lucknow (11.69%), Kanpur (11.32%), Pune (10.90%), Mumbai (8.68%), Ghaziabad (8.24%), Patna (7.66%), Bengaluru (6.96%), Jaipur (6.86%), Kolkata (6.78%), Delhi (6.70%), Indore (6.40%), Ahmedabad (3.35%), Nagpur (3.22%), Kozhikode (2.01%), Coimbatore (1.00%), Surat (0.99%), Kochi (0.72%) and Chennai (0.48%). National average for crime against women out of total crime is 7%



**Types of crime against women in metropolitan India :** The nature and intensity of crime against women in India have changed over time. Ancient Indian society was ideal in which women enjoyed respectable place. In medieval age several social ills (*sati prathe, dahej prathe*, ban on widow marriage, child marriage, polygamy and sexual exploitation of devdasi) paralyzed the equal status and freedom of women in India. Though, rejuvenation of Indian social system by different social activists during British period, legal action against anti-social and unethical practices by governments together with increased participation of women in socio-economic, administrative, academic and political system has considerably changed the status of women in postmodern society. But rate of crime against women is still increasing every year. Different types of crime committed against women in metropolitan cities of India has been classified by Indian Penal Code (IPC) as; Dowry death (Sec. 304, IPC), Abetment of suicide of women (Sec. 306, IPC), Causing miscarriage without women's consent (Sec. 313, IPC), Acid attack or attempt of acid attack (Sec. 326 A or B, IPC), Cruelty by husband or his relatives (Sec. 498, IPC), Kidnapping and abduction of women (Sec. 363 to 369, IPC), Human trafficking (Sec. 370, IPC), Rape or attempt of Rape (Sec. 376, IPC), Unnatural offences (Sec. 377, IPC), Assault on women with intent to outrage her modesty (Sec. 354, IPC) and Insult to modesty of women (Sec. 509, IPC). Among these crimes in metropolitan India, rate of crime is highest for cruelty by husband or his relatives (22.6) followed by assault on women with intent to outrage her modesty (19.3), kidnapping and abduction of women (17.1), rape or attempt of rape (9.4), insult to modesty of women (3.5), dowry death (0.9), abetment of suicide of women (0.7), unnatural offences (0.2), causing miscarriage without women consent (0.2), acid attack or attempt of acid attack (0.1), and human trafficking (0.1).

**Cruelty by husband or his relatives :** It is the most common crime in metropolitan cities of India with the rate of 22.6 incidences per lakh of women population. Highest rate of crime associated with cruelty by husband or his relatives has been observed in Jaipur (69.5) followed by Lucknow (64.9), Delhi (48.1) and Ghaziabad (43.7). In Coimbatore (3.5), Chennai (4.1), Mumbai (6.9) and Surat (9.9) [Table-2] rate of incidence of cruelty by husband or his relatives is relatively lower. The averaged rank score for this crime in metropolitan cities of north, central and south India are 5, 10.75 and 14. It means, incidences of cruelty by husband or his relatives is most common in metropolitan cities of north India followed by central and south Indian metro cities. The main reason behind this spatial difference is lower women empowerment in northern India followed by central and southern India, and high unemployment rate in metro cities of northern and central India (**Hindustan Times, 6 April 2017**).

**Assault on women with intent to outrage her modesty :** It is the second most common crime against women of metropolitan cities in India. Rate of incidence of assault on women with intent to outrage her modesty in metropolitan cities of India is 19.3 per lakh women population. Delhi (49.4), Nagpur (33.7), Lucknow (29.9) and Pune (27.7) have high rate for this crime on the other hand Chennai (1.5), Coimbatore (1.8), Surat (2.8) and Ahmedabad (4.4) have low rate of incidence of assault on women with intent to outrage her modesty (**Table-2**). Averaged rank score for metro cities of north, central and south India are 8.14, 9.75 and 11 respectively. Therefore, as we move northward intensity of incidence of this crime increases in metro cities of India. The main reason behind this spatial difference is high rate of unemployment in metropolitan cities of north and central India and poor social status of women in these cities (Mukherjee, Rustagi and Krishnaji, 2001).

**Kidnapping and abduction of women :** Kidnapping and abduction of women is third most common illegal practice against women in metropolitan cities of India. On an average, seventeen out of one lakh women population were kidnapped or abducted in metro cities of India in 2016. Highest rate of kidnapping of women has been observed in Patna (56.9) followed by Delhi (41.1), Lucknow (33.6) and Nagpur (30.6). Female foeticide (67.6) and lowest in Pune (9.1). Hence low rate of women kidnapping (Table-2) in metro cities of north, central and south Indian metro cities are 6, 9.25 and 13.88 respectively. It means south Indian metropolitan cities have relatively low rate of women kidnapping and abduction and as we move northward rate of kidnapping and abduction of women in metro cities increases. Major unemployment problem in north and central Indian metro cities is the main reason behind higher rate of kidnapping of women here.

**Rape or attempt of rape :** The fourth most common crime against women in metropolitan cities of India is rape or attempt to rape. Rate of rape incidence in metro cities of India is about nine per one lakh women population. The rate of gang rape and attempt to rape women in these cities are 0.3 and 0.1 respectively. Custodial rape is not a common phenomenon in these cities. Only one such case was recorded in Delhi and Ahmedabad in 2016. Highest rate of rape or attempt of rape has been recorded in Delhi (26.7) followed by Jaipur (23.1), Indore (17.4) and Pune (14.8) and it is lowest for Coimbatore (0) followed by Kolkata (0.2), Chennai (0.6), Ahmedabad and Kanpur (3.6) [Table-2]. Averaged rank score for rape and attempt of rape in metro cities of northern, central and south Indian states are 8.7, 8.25 and 11.25 respectively. So, intensity of rape incidences are lowest in metro cities of south India, and northern and central Indian metro cities have almost equal intensity of rape. Women empowerment in southern states has a great deal with this spatial variation.

**Insult to modesty of women :** In year 2016 total 1917 incidence of insult to modesty of women has been recorded in metropolitan cities of India with the rate of 3.5 per lakh women population. So, it is not among common crimes against women in metropolitan India. Highest rate of this crime was recorded in Delhi (10.3) followed by Indore (8.8), Hyderabad (5.5) and Mumbai (5). In Coimbatore, Jaipur, Lucknow and Surat no such cases were recorded and rate of insult to modesty of women is zero here (Table-2). If we find spatial variation in intensity of this crime on the basis of averaged rank score it is highest for south Indian metro cities (averaged rank score of 7.5) followed by central (averaged rank score 8.5)and north (averaged rank score 8.86) Indian metro cities. Greater participation of women in socio-economic, administrative and political system makes women more vulnerable to this crime in south Indian metros (Mukherjee, Rustagi and Krishnaji, 2001).

**Dowry death :** Though dowry death is not very common crime against women in metro cities of India but it has large impact on our society. Rate of dowry death in metropolitan cities of India is less than one per one lakh women population. Dowry is an economic burden on father of women and compels them for female feticide. Deaths related to dowry badly affect relatives of men and women as well as society. Leading metro cities of India in terms of rate of dowry death are Patna (7.9), Kanpur (3.7), Lucknow (3) and Jaipur (2.1). Surat (0), Chennai, Coimbatore, Ahmedabad, Kochi and Kolkata (0.1) have least rate of dowry deaths (Table-2). Averaged rank score calculated for northern, central and south Indian metro cities are 4.57, 9.25 and 9.75 respectively. So, intensity of this crime is highest in metros of northern India followed by central and south Indian metros. This spatial variation in rate of dowry death is due to lesser participation of women in work and politics, and particular social practices in northern India.

**Abetment of suicide of women** : Abetment to commit suicide by women is treated the most uncommon crimes in metro cities of India as the rate of this crime ranges only to 7 incidences per one lakh women population in concerned cities. Nagpur (2.6), Indore (2.6), Bengaluru (1.9) and Pune (1.6) are some of the cities where rate of abetment of suicide of women is relatively high. On the other hand it is nil (0) for Coimbatore, Ghaziabad, Kochi, Kozhikode, Lucknow and Patna (Table-2). Averaged rank score for this crime in metropolitan cities of north India is 8.7. It is 4.5 and 7.1 respectively for metro cities of north, central and south India. So, central Indian metro cities have higher intensity of this criminal activity followed by metro cities of south and north India. Higher intensity of abetment of suicide by women in metro cities of south and central India is due to changing social order in advanced societies of India and mental pressure by the abettor.

**Other crimes against women** : Unnatural offences and causing miscarriage without women consent (0.2 per one lakh women population), and acid attack or attempt of acid attack and human trafficking (0.1 per one lakh women population) are some other types of crime against women in metro cities of India. Rate of these crimes are significantly lower than other crimes against women. These criminal incidences are localized, have been recorded in very few metro cities. Sixty five Cases of unnatural offences has been recorded in Lucknow, 23 cases in Delhi, 11 cases in Mumbai, 2 cases in Ahmedabad, Hyderabad, Nagpur and Pune, and one case has been recorded in Indore. 85 cases of miscarriage without women consent have been recorded in Lucknow and one such has been recorded in Bengaluru. 18 incidences of acid attack has been recorded in Delhi, 3 cases in Ahmedabad, 2 cases in Kolkata, and one case in Ghaziabad, Indore, Jaipur, Kanpur, Nagpur and Pune. Kolkata (10 cases), Delhi (9cases), Kochi (6 cases), Bengaluru (4 cases), Nagpur (3 cases), Chennai, Ghaziabad and Hyderabad (1 case) are some of the metro cities in India where some cases of human trafficking has been recorded. Aforementioned four crimes against women are more intense in north Indian metropolitan cities followed by central and south Indian metro cities. The reason behind this spatial variation is more women empowerment in south Indian cities than their northern counterpart, socio-economic differences and higher rate of unemployment in metro cities of north India as compared to south and central Indian metros.

**Conclusion** : Crime against women is a common phenomena but the intensity of crime against women in metropolitan India is lower than that of overall crime in the study area. The rate of crime against women in metropolitan cities of India is 77.2 crime incidences per one lakh women population. The most common and intense illegal practice against women in metro cities of India is cruelty by husband or his relatives, followed by assault on women with intent to outrage her modesty, kidnapping and abduction, rape or attempt of rape, insult to modesty of women, dowry death, abetment of suicide by women, unnatural offence, causing miscarriage without women consent, human trafficking and acid attack. On average metropolitan cities in northern India have high rate of crime against women followed by metro cities in central India. Metro cities of southern India have lowest crime rate against women. Dowry death, miscarriage without women consent, cruelty by husband or his relatives, kidnapping and abduction and assault on women with intent to outrage her modesty are crimes against women whose intensity is maximum in metro cities of north India. Intensity of crimes like, abetment of suicide of women, acid attack or attempt to acid attack and rape or attempt of rape is highest in metro cities of central India. Human trafficking and insult to modesty of women are more intense criminal activities in metro cities of south India. On the basis of recorded data (in 2016) of crime against women in metropolitan cities of

dia. Coimbatore in Tamilnadu is safest city for women and Delhi is the most dangerous city for them.

Table-1

Crime against women in metropolitan cities of India: overall statistics (2016)

| Name of Metropolitan city | Total number of crime | Number of crime against women | Crime against women (as percentage of total crime) | Crime rate (number of crime per lakh women population) | Rank (on the basis of crime rate) |
|---|---|---|---|---|---|
| Ahmedabad | 31762 | 1126 | 3.55 | 37.5 | 13 |
| Bengaluru | 49038 | 3412 | 6.96 | 84.0 | 9 |
| Chennai | 113847 | 544 | 0.48 | 12.6 | 12 |
| Coimbatore | 10205 | 102 | 1.00 | 9.5 | 19 |
| Delhi | 206135 | 13803 | 6.70 | 182.1 | 1 |
| Ghaziabad | 12518 | 1031 | 8.24 | 93.7 | 7 |
| Hyderabad | 18295 | 2419 | 13.22 | 64.3 | 11 |
| Indore | 16473 | 1055 | 6.40 | 101.4 | 6 |
| Jaipur | 30477 | 2090 | 6.86 | 144.1 | 3 |
| Kanpur | 9272 | 1050 | 11.32 | 78.4 | 10 |
| Kochi | 54125 | 392 | 0.72 | 36.3 | 14 |
| Kolkata | 24956 | 1693 | 6.78 | 24.9 | 17 |
| Kozhikode | 17491 | 352 | 2.01 | 33.2 | 15 |
| Lucknow | 18869 | 2205 | 11.69 | 159.3 | 2 |
| Mumbai | 59072 | 5128 | 8.68 | 60.2 | 12 |
| Nagpur | 42866 | 1379 | 3.22 | 113.0 | 5 |
| Patna | 16769 | 1284 | 7.66 | 133.8 | 4 |
| Pune | 19554 | 2131 | 10.90 | 89.2 | 8 |
| Surat | 56943 | 565 | 1.00 | 28.7 | 16 |
| Total | 808637 | 41761 | 5.16 | 77.2 | |

Source: National Crime Record Bureau report, 2016.

Table-2

Crimes against women in metropolitan cities of India (2016)

| Name of metropolitan city | Dowry death | | Abetment Of suicide of women | | Causing miscarriage without women's consent | | Acid attack or attempt of acid attack | | Cruelty by husband or his relatives | | Kidnapping Or abduction of women | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | R | I | R | I | R | I | R | I | R | I | R |
| Ahmedabad | 02 | 0.1 | 21 | 0.7 | 00 | 0.0 | 01 | 0.1 | 562 | 18.7 | 271 | 9.0 |
| Bengaluru | 57 | 1.4 | 76 | 1.9 | 01 | 0.0 | 00 | 0.0 | 489 | 12.0 | 674 | 16.6 |
| Chennai | 05 | 0.1 | 37 | 0.9 | 00 | 0.0 | 00 | 0.0 | 178 | 4.1 | 15 | 0.3 |
| Coimbatore | 01 | 0.1 | 00 | 0.0 | 00 | 0.0 | 00 | 0.0 | 37 | 3.5 | 04 | 0.4 |
| Delhi | 144 | 1.9 | 20 | 0.3 | 00 | 0.0 | 18 | 0.2 | 3645 | 48.1 | 3364 | 44.4 |
| Ghaziabad | 20 | 1.8 | 00 | 0.0 | 00 | 0.0 | 01 | 0.1 | 481 | 43.7 | 235 | 21.4 |
| Hyderabad | 18 | 0.5 | 30 | 0.8 | 00 | 0.0 | 00 | 0.0 | 1311 | 34.0 | 227 | 6.0 |
| Indore | 19 | 1.8 | 25 | 2.4 | 00 | 0.0 | 01 | 0.1 | 278 | 26.4 | 330 | 32.1 |
| Jaipur | 31 | 2.1 | 09 | 0.6 | 00 | 0.0 | 01 | 0.1 | 1008 | 69.8 | 477 | 33.0 |
| Kanpur | 50 | 3.7 | 12 | 0.9 | 00 | 0.0 | 01 | 0.1 | 365 | 27.2 | 445 | 33.1 |
| Kochi | 01 | 0.1 | 00 | 0.0 | 00 | 0.0 | 00 | 0.0 | 111 | 10.3 | 65 | 6.1 |
| Kolkata | 10 | 0.1 | 21 | 0.3 | 00 | 0.0 | 02 | 0.0 | 886 | 11.9 | 124 | 1.7 |
| Kozhikode | 02 | 0.2 | 00 | 0.0 | 00 | 0.0 | 00 | 0.0 | 161 | 15.3 | 06 | 0.6 |
| Lucknow | 42 | 3.0 | 00 | 0.0 | 85 | 6.2 | 00 | 0.0 | 895 | 64.8 | 601 | 43.6 |
| Mumbai | 12 | 0.1 | 27 | 0.3 | 00 | 0.0 | 00 | 0.0 | 582 | 6.9 | 1142 | 13.4 |
| Nagpur | 06 | 0.5 | 32 | 2.6 | 00 | 0.0 | 01 | 0.1 | 248 | 20.1 | 368 | 29.7 |
| Patna | 76 | 7.9 | 00 | 0.0 | 00 | 0.0 | 00 | 0.0 | 105 | 12.2 | 382 | 38.5 |
| Pune | 10 | 0.4 | 38 | 1.6 | 00 | 0.0 | 01 | 0.1 | 329 | 15.9 | 578 | 24.7 |
| Surat | 00 | 0.0 | 12 | 0.6 | 00 | 0.0 | 00 | 0.0 | 195 | 9.9 | 162 | 8.2 |
| Total | 506 | 0.9 | 360 | 0.7 | 86 | 0.2 | 29 | 0.1 | 12218 | 23.6 | 9256 | 17.1 |

Source: National Crime Record Bureau report (2016); I- Number of incidence, R- rate of crime (per lakh women).

Table- 2 : Crimes against women in metropolitan cities of India (2016)

| Name of metropolitan city | Human Trafficking | | Rape or attempt of rape | | Incidence of offences | | Assault on women with intent to outrage her modesty | | Insult to modesty of women | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I | R | I | R | I | R | I | R | I | R |
| Ahmedabad | 00 | 0.0 | 112 | 3.7 | 02 | 0.1 | 131 | 4.4 | 62 | 0.3 |
| Bengaluru | 04 | 0.1 | 324 | 8.0 | 00 | 0.0 | 820 | 20.3 | 54 | 1.3 |
| Chennai | 01 | 0.0 | 25 | 0.6 | 00 | 0.0 | 63 | 1.5 | 03 | 0.1 |
| Coimbatore | 00 | 0.0 | 00 | 0.0 | 00 | 0.0 | 12 | 1.2 | 00 | 0.0 |
| Delhi | 09 | 0.1 | 2025 | 26.7 | 23 | 0.3 | 3746 | 49.4 | 783 | 10.3 |
| Ghaziabad | 01 | 0.1 | 117 | 10.6 | 00 | 0.0 | 172 | 15.6 | 61 | 5.5 |
| Hyderabad | 01 | 0.0 | 170 | 4.5 | 02 | 0.1 | 387 | 10.3 | 205 | 5.5 |
| Indore | 00 | 0.0 | 181 | 17.4 | 01 | 0.1 | 222 | 21.3 | 92 | 8.8 |
| Jaipur | 00 | 0.0 | 334 | 23.1 | 00 | 0.0 | 301 | 20.8 | 69 | 4.8 |
| Kanpur | 00 | 0.0 | 55 | 4.1 | 00 | 0.0 | 154 | 11.5 | 01 | 0.1 |
| Kochi | 06 | 0.6 | 62 | 5.8 | 00 | 0.0 | 162 | 15.0 | 23 | 2.1 |
| Kolkata | 10 | 0.1 | 18 | 0.2 | 00 | 0.0 | 348 | 3.1 | 243 | 2.1 |
| Kozhikode | 00 | 0.0 | 52 | 4.9 | 00 | 0.0 | 109 | 10.3 | 19 | 1.8 |
| Lucknow | 00 | 0.0 | 102 | 7.4 | 65 | 4.7 | 412 | 29.9 | 00 | 0.0 |
| Mumbai | 00 | 0.0 | 713 | 8.4 | 11 | 0.1 | 2183 | 25.6 | 425 | 5.0 |
| Nagpur | 03 | 0.2 | 171 | 14.0 | 02 | 0.2 | 411 | 33.7 | 04 | 0.3 |
| Patna | 00 | 0.0 | 63 | 6.5 | 00 | 0.0 | 102 | 10.6 | 03 | 0.3 |
| Pune | 00 | 0.0 | 354 | 14.8 | 02 | 0.1 | 661 | 27.7 | 56 | 2.3 |
| Surat | 00 | 0.0 | 121 | 6.1 | 00 | 0.0 | 55 | 2.8 | 00 | 0.0 |
| Total | 35 | 0.1 | 4999 | 9.2 | 108 | 0.2 | 10458 | 19.3 | 1917 | 3.5 |

Source: National Crime Record Bureau report (2016); I- Number of incidence, R- rate of crime (per lakh women).

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# Biological, Electronic, NLO, NBO, TDDFT and Vibrational Analysis of 1-benzyl-4-formyl-1H-pyrrole-3-carboxamide

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**ABSTRACT:** *Biological Electronic, Optical Properties and Vibrational Analysis of 1-benzyl-4-formyl-1H-pyrrole 3carboxamide are studied by using a combination of DFT/B3LYP method and 6-311G (d, p) basis set. Optimized parameters of the title molecule are well-matched with the experiments. The NLO properties of 1-benzyl-4-formyl-1H-pyrrole 3carboxamide have been examined with the help of Polarizability and Hyper-Polarizability. The electronic properties of 1-benzyl-4-formyl-1H-pyrrole 3carboxamide are described with the help of HOMO, LUMO composition. The UV spectra suggest that a strong excitation line occurs at 2.03 eV (160 nm) due to H-2→LUMO (30%). NBO analysis shows that hyper conjugative interaction energy has higher value during LP→ π*, π→ π* transitions. Several biological activities are calculated by PASS software. Docking of the molecule is performed with 5P4Q protein and FF score is -1051.65A.U.*

**KEYWORDS:** *Vibrational analysis; NBO; NLO; DFT; Electronic properties; PASS.*

## INTRODUCTION

Quantum Chemical calculations give important information about molecular geometry, vibrational frequency, electronic properties, UV spectra analysis as well as NLO properties of a molecule. [1-2] Benzyl is the substituent possessing the benzene ring attached to a $CH_2$ group ($C_6H_5CH_2$-). [3] The position of the first carbon bonded to benzene or another aromatic ring is described as benzyl. The 4-formyl-1H-pyrrole-3 carboxamide is a heterocyclic aromatic organic compound in which three hydrogen of Pyrrole ring (five-membered) replaced by formyl, carboxamide, and Benzyl group. Heterocyclic compounds are those cyclic compounds that contain at least two different elements as 'ring members' atoms. These compounds are organic or inorganic, within the ring structure containing one carbon atom, and one or more atoms of elements other than carbon, such as sulphur, oxygen, nitrogen, etc. Simple N heterocycles have acknowledged significant consideration because o

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*1021-9986/2020/1/233-242 10/$/6.00*

Research Article

their important biological properties and their role as pharmacophores. [4.] The introduction of acyl group on nitrogen atom of pyrrole possesses medicinal importance. [5]. In chemistry, formylation is termed as addition of formyl functional group. Formylation has been identified in several critical biological processes [6]. Pyrrole rings have pharmacological as well as biological implications [7]. The derivatives of Pyrroles are very important in drug discovery. [8] These derivatives are used as pharmacological activity such as anti-inflammatory [9], antibacterial [10-13], antioxidant [14] and antitumour agents [15]. Qi-Di Zhong etal. synthesized new pyrrole derivatives 1-benzyl-4-formyl-1H-pyrrole 3carboxamide with good biological activities, and also reported its crystal structure. The present work on 1-benzyl-4-formyl-1H-pyrrole 3carboxamide has been carried out to support and as an extension of the work of Qi-Di *Zhong et al.* [16] In this paper we perform a complete quantum chemical study of 1-benzyl-4-formyl-1H-pyrrole 3carboxamide by using combination DFT/B3LYP method and 6-311G (d, p) basis set. To verify its biological activity several biological activities have been calculated using PASS software and docking is performed by appropriate target.

***Computational Methods***

Initial geometry of the molecule is modeled with the help of Gauss View 5.0 by using slandered parameters. Geometry optimization is done without any constraint in the potential energy surface. The gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [17] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [18] has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, by using GAUSSIAN 09 [19]. Vibrational frequency assignments were made with a high degree of accuracy by combining the results of the GAUSSVIEW'S program [20] with symmetry considerations. In this study, 6-311G(d, p) basis set with d polarization function for heavy atoms and p polarization function for hydrogen atom is used. 6-311G(d, p) basis set gives better description of polar bond in our study. [21-22] Natural bond analysis is calculated by NBO3.0 program package [23].

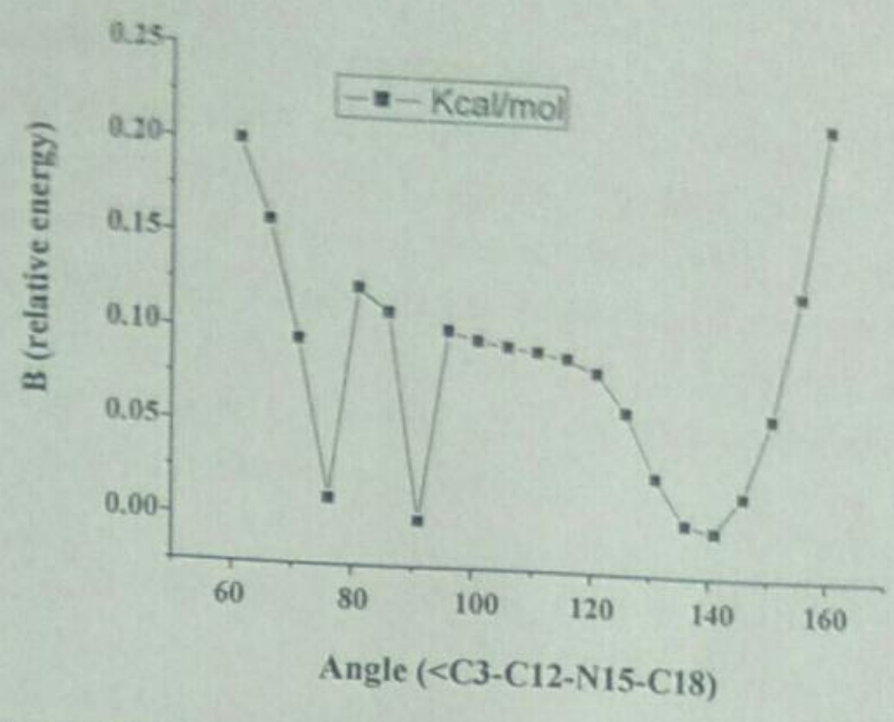


*Fig. 1: PES Scan of dihedral angle <3C-12C-15N-18C with 20 step each of 5⁰.*

## RESULTS AND DISCUSSIONS

***Optimization***

The local minimum energy obtained by structure optimization of the molecule is approximately 716.02957909 A.U. Animated gauss view picture shows that the molecule has no point group symmetry. For optimized parameters bond length is measured in $A^0$ and bond angle in degrees. To obtain global minima we scan dihedral angle <3C-12C-15N-18C with 20 step each of $5^0$ and then plot a graph (Fig. 1) in between relative energy and dihedral angle. From this plot, conformer with dihedral angle <3C-12C-15N-18C = 91.147 $^0$ (shown Fig. 3) has the lowest energy. This conformer has 0.01041 kcal/mol lower energy than next stable conformer with<3C-12C-15N-18C = $76.147^0$. For sake of simplicity we have considered the most stable conformer for our study. In the molecule there are two rings namely pyrrole and benzyl rings, nearly perpendicular, are connected with methyl group. The calculated geometry parameter are compare with experimental data in Supplementary Table 1. The calculated (C-N) bond length, lies in between 1.3976Å- 1.3488Å, is in agreement with experimental results [16](1.37Å -1.36Å) while calculated (N-H) bond length lies in between 0.9973Å- 0.9937Å, which matches with experimental value (1 Å). The C-O bond length is found to be 1.37 Å however experimental value is 1.29 Å. In Fig. 2 we plot a graph between experimental and calculated bond length of the molecule. Graph shows linear relation and after linear correlation between experimental bond lengths with calculated bond length by DFT method we find correlation equation

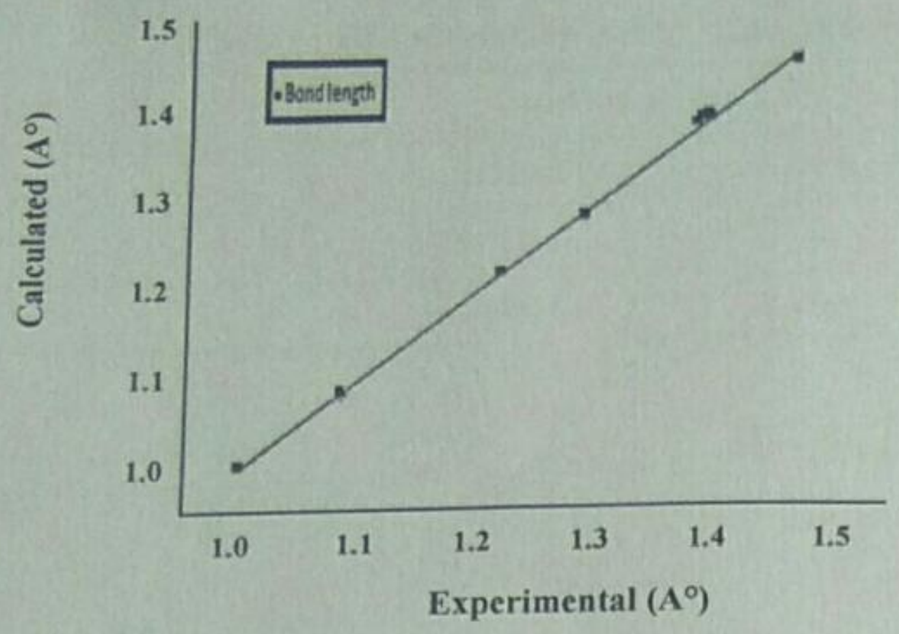


*Fig. 2: Comparison between experimental and theoretical bond length.*

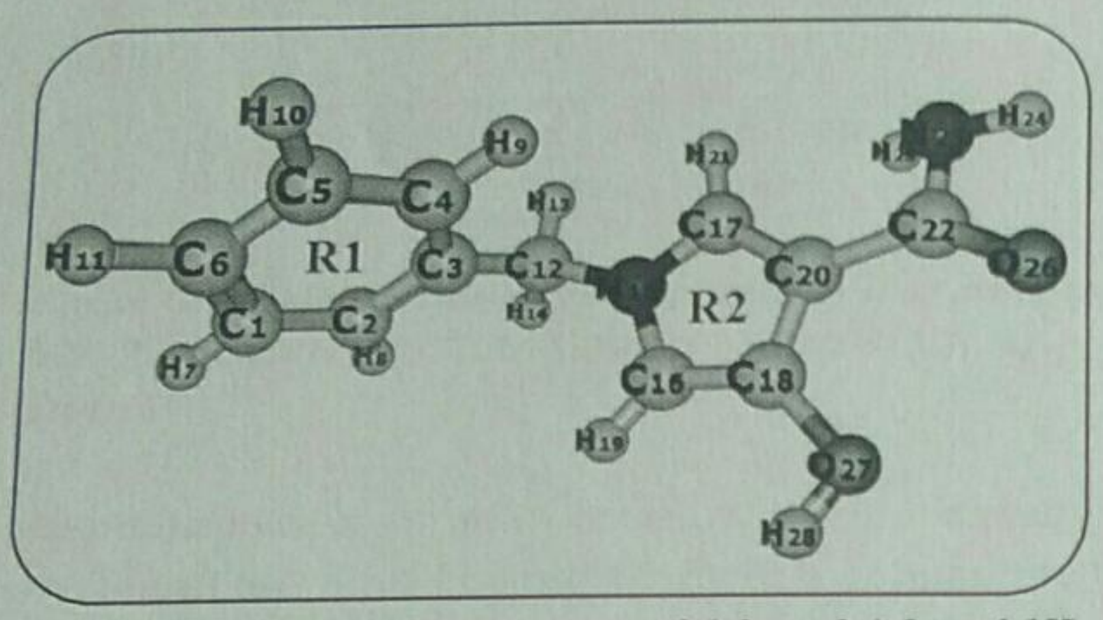


*Fig. 3: Model molecular structure of 1-benzyl-4-formyl-1H-pyrrole-3carboxamide.*

Calculated = 0.98062 experimental + 0.01911 with correlation factor $R^2$=0.99861.

The correlation factor >0.99 shows that the DFT can reproduce experimental result well. The angular changes in benzene ring geometry have proved to be a sensitive indicator of the interaction between the substituent and the attached ring. The (C-N-C) bond angle varies from $124.82^0$- $109.40^0$ while (C-N-H) varies between $181.07^0$-$123.24^0$.

***Polarizability, Hyper polarizability and thermodynamic properties***

The Dipole moment (μ), polarizability <α> and total first static hyper polarizability β are used to determine NLO property of title molecule.[24-25] These parameter are calculated by using combination of DFT/B3LYP method and 6-311G(d, p) basis set (supplementary Table-2). First order hyperpolarizability is a third rank tensor of 3×3×3 matrix. By using Kleinman symmetry, consideration 27 components of the 3-D matrix can be reduced to 10 components.[26] Polarizability and hyperpolarizability belongs to first and higher order derivatives of the electron density which is helpful to determine shape and interaction characteristics of chemical bond in molecule. These parameter can be expressed in terms of *x*, *y*, *z* components and are given by following equations 1, 2,3

$$\mu = \left(\mu_X^2 + \mu_Y^2 + \mu_Z^2\right)^{1/2} \quad (1)$$

$$<\alpha> = 1/3\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right] \quad (2)$$

$$\beta_{Total} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2} \quad (3)$$

The β components of Gaussian output are reported in atomic units.

Where (1 a.u. = $8.3693X10^{-33}$ e.s.u.).

For 1-benzyl-4-formyl-1H-pyrrole-3carboxamide molecule, calculated dipole moment value is 4.2863 Debye which is greater than dipole moment of water (2.16 Debye), is attributed to electron withdrawing group –COONH2- and –OH- group present on hetro-cyclic ring. From supplementary Table 2 we see higher contribution of axial component in polarizibility shows that molecule is elongated more towards axial direction. In hyperpolarizibilty $\beta_{xxx}$, $\beta_{xzz}$ component having larger contribution shows that a larger electron density along bond along X direction and XZ plane. This shows that X axis and XZ plane are more optical active directions. The calculated values for the total intrinsic hyperpolarizability $\beta_{TOTAL}$ and the component of the hyperpolarizability ($\vec{\beta}$) are given in supplementary Table 2. The calculated value $\beta_{TOTAL}$ of title molecule ($0.9339x10^{-30}$ e.s.u.) is nearly five times greater than hyperpolarizibilty of urea ($0.19347x10^{-30}$e.s.u.) so title molecule use as NLO active molecule

***Thermodynamical Properties***

Thermodynamic properties like entropy, enthalpy and heat capacity at various temperatures (100-400 K) have been calculated (Fig. 4) by DFT/6-311G(d, p) method from the theoretical vibration analysis. These parameters increase with temperature. The graphs between

***Table 1: The observed UV-vis spectra are calculated by TD-DFT method at B3LYP/6-311 G (d, p) level.***

| Excitation energy (eV) | wavelength (nm) | | Oscillator strength | Orbital transition |
|---|---|---|---|---|
| | Calculated | Assignment | | |
| 4.12 | 250.62 | $n\rightarrow\pi^*$ | 0.0008 | H-4->L+1 (26%) |
| 2.03 | 160.20 | $\pi\rightarrow\pi^*$ | 0.2305 | H-2->LUMO (30%) |

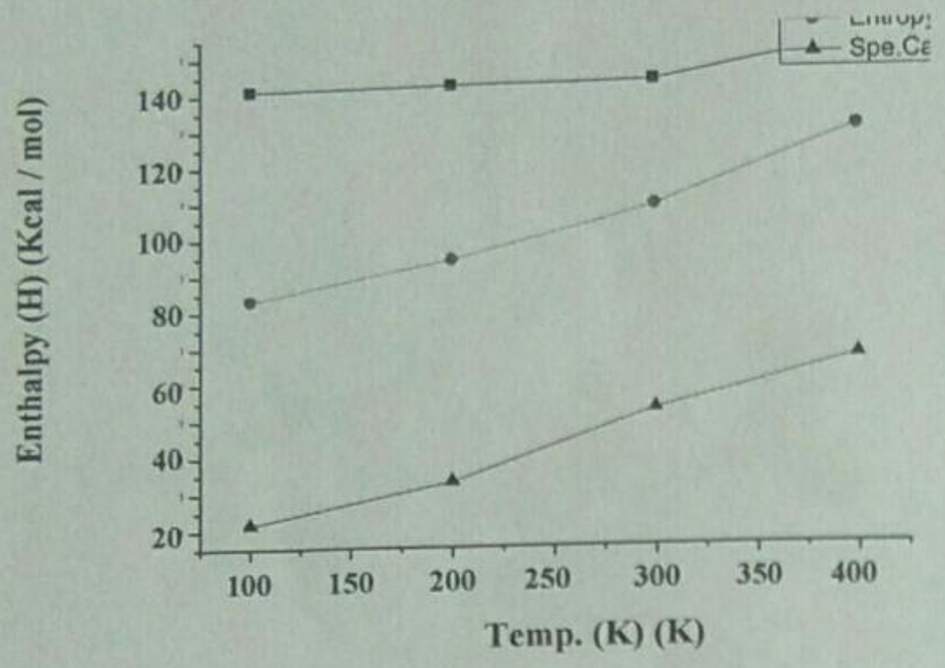


***Fig. 4: Graph plotted between entropy enthalpy Heat capacity V/S Temperature (K) calculated by DFT/6-311G (d, p) method.***

temperature-entropy and enthalpy -heat capacity are plotted and fitted in quadratic formula of order two. The fitting factors for these calculated thermodynamic properties are 0.97519 (for C), 0.99873 (S) and 0.9899 (H), respectively, while the second order quadratic fitting equations are as follows

$H^0_m=147.1585-0.07799T+.000221T^2$ ($R^2=0.9899$)

$C^0_{p.m}=8.503+0.11861T+0.000067T^2$ ($R^2=0.97519$)

$S^0_m=78.14075+0.02638T+0.000247T^2$ ($R^2=0.99873$)

These quadratic equations give significant information about thermochemical field to calculate thermodynamic energy.

***Electronic Properties and UV Spectra***

The interaction of the molecule with other chemical system is resolute by frontier orbitals, FHOMO and FLUMO which can be verified by experimental data. The frontier orbital gap is equal to HOMO-LUMO gap which helps to determine the kinetic stability and chemical reactivity of the molecule. The molecule is termed as soft molecule when it becomes more polarizable, high chemically reactive, low kinetically stabile and have small frontier orbital gap. [27] The frontier orbital gape calculated for given molecule is 6.20 eV, shows molecule is less chemically active. The contour plots of HOMO, LUMO orbital and MESP of the molecule are shown in Fig. 4. In this plot HOMO, which primarily acts as donor is distributed over $R_2$ ring of the molecule while LUMO behaves as acceptor distributed over benzene ring. The transition from HOMO→LUMO shows that charge is transferred from ring $R_2$ to benzene ring.

The MESP plot gives valuable information about reactive site to positive, negative, and neutral electrostatic potential region in terms of color coding e.g red as electro negative, blue as electro positive and yellow as neutral site[28-30]. MESP of the molecule visibly suggests that the major electronegative potential region (shaded with Red colour) $O_{27}$, $O_{26}$ atoms of –CONH2- group and most electropositive region $C_{22}$ (shaded with blue colour).

***UV spectra TDDFT analysis***

Time dependent density theory is important tool for the study of the nature of transition of electron in title compound. After optimization by using combination of DFT/B3LYP method and 6-311G (d, p) basis set, we have used TD-DFT calculation with same level theory to find energy of various transition state. The calculated electronic transition energies (Table 1) at 4.12 eV (250.62 nm) and 2.0 3eV (160.20 nm) mainly originate due to H-4→L+1(26%), H-2→LUMO(30%) transitions respectively. The plot and transition of HOMO-4(MO=53), H-2(MO=55), LUMO (MO=58) LUMO+1(MO=59) of the molecule is shown in Fig. 6. HOMO-2 is localized over Benzene ring (as HOMO) however HOMO-4 is localized over $–CONH_2$-group. The LUMO and LUMO+1 are nearly localized over whole molecule. So the transitions from H-4→L+1 and H-2→LUMO show that charge transfer from benzene and $–CONH_2$- group to $R_2$ ring. A graph is plotted between wavenumber and oscillatory strength and shown in Fig. 5. On the basis of the calculated molecular orbital coefficients analyses electronic transition are assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ respectively.

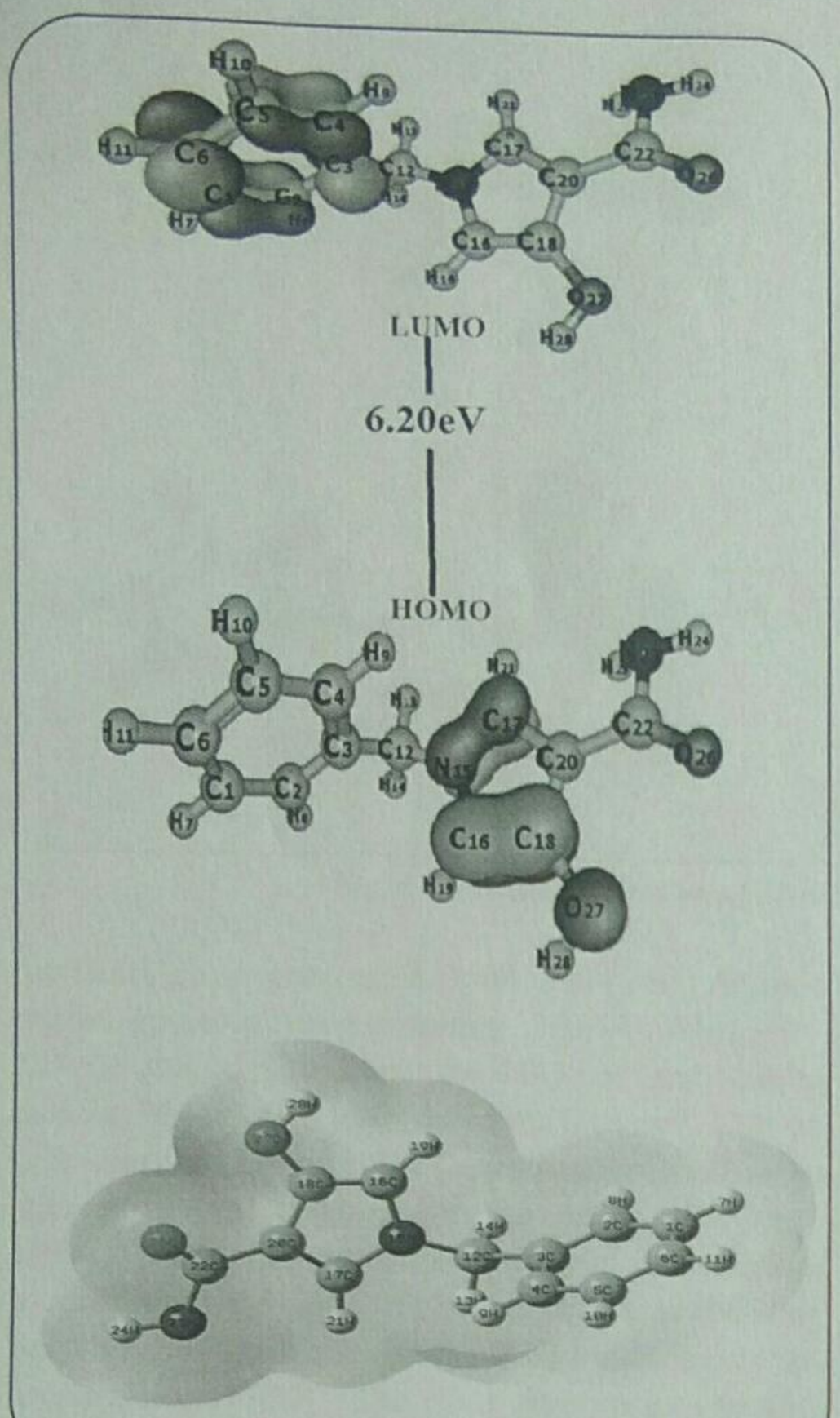


*Fig. 4: HOMO - LUMO MESP pictures of 1-benzyl-4-formyl-1H-pyrrole-3carboxamide*

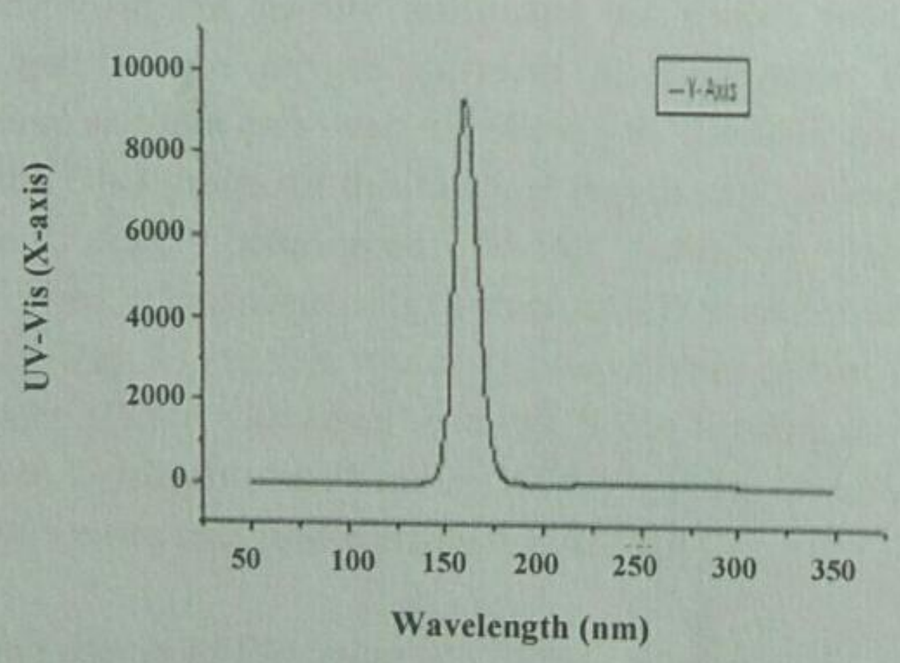


*Fig. 5: Calculated UV spectra of Title molecule using combination of DFT/B3LYP method and 6-311G(d,p) basis set.*

### *Assignments of Fundamentals*

In 1-benzyl-4-formyl-1H-pyrrole-3-carboxamide has 28 atoms 78 normal modes of vibration. The assignments of the calculated wave numbers are based on animated view of normal mode and listed in supplementary Table 3. The calculated frequencies are typically higher than the experimental one due to combination of electron correlation and anharmonicity. [31-32] Due to this reason thr theoretical frequency is scaled. Vibrational frequencies is scaled by the factor of 0.96 [33]. Some important modes of vibrations are discussed here.

### *Vibrational modes discription*

*Ring vibration*

The presence of C–H stretching vibrations in the region 2800–3100 $cm^{-1}$, which is the characteristic region for identification of the C–H group.[33] In the molecule the C-H functional group is present at a number of positions. Three medium intense polarized peaks with polarization vectors directed along ring $R_1$ appear at 3231 $cm^{-1}$, 3240 $cm^{-1}$ and 3251 $cm^{-1}$ due to ν(C–H) R1. Two medium intense polarized peaks lying on lower side of spectral region due to β (C-H) $R_1$ and γ (C-H) $R_1$ are at 1562 $cm^{-1}$ ,778 $cm^{-1}$ respectively. An intense and a medium intense peaks occur due to mixing of ν(C=C) $R_1$, β (C-H)$R_1$ corresponding to 1743 $cm^{-1}$ and 1562 $cm^{-1}$ respectively. A very intense peak occurs due to mixing of in plane $O_{27}$-$H_{28}$ bending $C_{16}$-$N_{15}$ stretching in ring $R_2$ is at 1470 $cm^{-1}$. The μ($C_{16}$-$N_{15}$) appears as a prominent mode in the FT-IR spectra at 1686 $cm^{-1}$. Three back to back sharp peak appears due to stretching of $C_{16}$-$N_{15}$ bond in ring $R_2$ appears at 1472 $cm^{-1}$1500 $cm^{-1}$ 1529 $cm^{-1}$ . A very weak intense peak appears at 1115 $cm^{-1}$ due to in plane bending $C_{16}$-$N_{15}$ -$C_{17}$ in ring $R_2$ however at lower range of spectra two intense peak appears due to γ ($C_{16}$-$N_{15}$ - $C_{17}$)$R_2$ appears at 928 $cm^{-1}$ and 684 $cm^{-1}$ respectively.

*-$CONH_2$-group vibration*

The $-NH_2$ and –C=O functional groups are noteworthy elements of the molecule and vibrations corresponding to these groups are present in a number of modes. The N-H stretching vibration generally obtained in the region of 3500-3000 $cm^{-1}$ [34]. In this study at higher frequency region two intense modes due to antisymmetric and symmetric stretching of $NH_2$ in $-CONH_2$

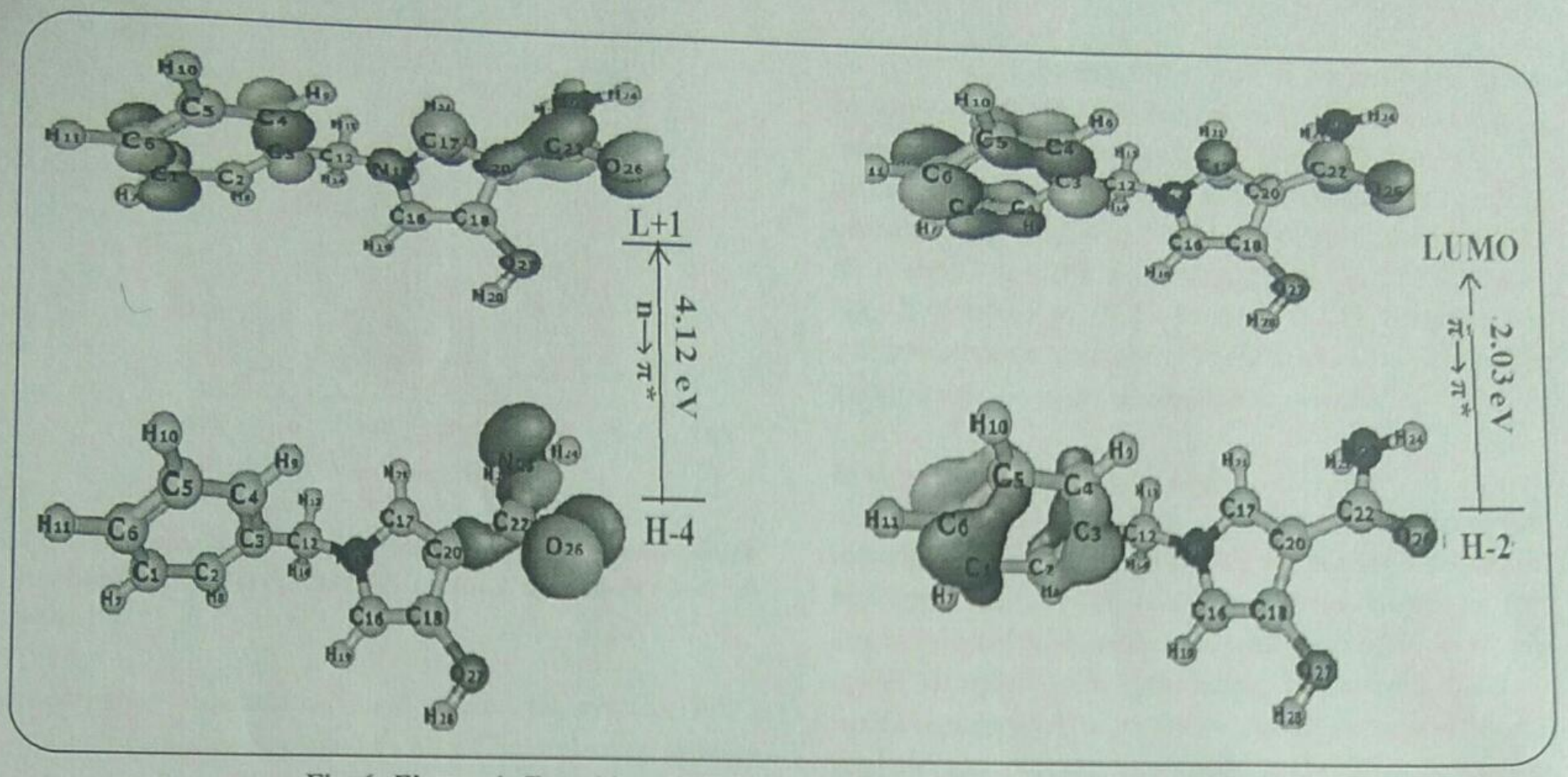


*Fig. 6: Electronic Transition of TD-DFT of title molecule by DFT/B3LYP method.*

functional group occur at 3637 $cm^{-1}$,3554 $cm^{-1}$. At lower region frequency two scissoring S($H_{24}$-$N_{23}$-$H_{25}$) of –$CONH_2$ group are 1682 $cm^{-1}$ and 1145 $cm^{-1}$ and wagging modes ω($H_{24}$-$N_{23}$-$H_{25}$) $R_2$ obtained are 1184 $cm^{-1}$, 1226 $cm^{-1}$, 856 cm-1 and 611 $cm^{-1}$. The C=O stretching band having high intensity is obtained in the region 1800 $cm^{-1}$-1650 $cm^{-1}$ [35.], however their exact position is governed by the inter and intra molecular hydrogen bonding, electronic and mass effects of adjacent substituents and conjugations [36-37]. The C-O stretching vibrations intensity increases the probability of formation of hydrogen bonds. The C=O bond is produced by $p_\pi$ - $p_\pi$ between carbon and oxygen atoms. In C=O bond bonding electron are not equally distributed but shifted towards oxygen because oxygen is more electronegative than carbon and lone pair electron of oxygen decides nature of the C=O group. In this study a very intense polarized band with polarization vector directed along the plane of adjacent ring occurs at 1785 $cm^{-1}$ due to μ($C_{22}$-$O_{26}$) $R_2$. In this stretching mode both carbon and oxygen vibrate with equal intensity. Some bending modes due to $C_{22}$-$O_{26}$in plane bending modes appears lower side of IR spectra with low intensity e.g. 627 $cm^{-1}$.

***Other Modes of Vibration***

Pulay *et al* [38] recommended the vibratuinal frequencies on the basis of *internal* coordinate system. $NH_2$ and $CH_2$ group connect with six types of vibrational frequencies namely: two stretching modes symmetric, asymmetric and rest four bending modes e.g., scissoring, rocking, wagging and twisting. In which two scissoring and rocking deformations belong to polarized in–plane vibration however wagging as well as twisting deformations belong to depolarized out–of–plane vibration.

In calculated spectra one low intense polarized peak with polarization vector is directed along $C_{17}$-$N_{15}$ at 3140 $cm^{-1}$ due to $\mu_{as}$($H_{14}$-$C_{12}$-$H_{13}$) adj $R_1$ and a medium intense peak occurs at 3097 $cm^{-1}$ due to symmetric $\mu_s$($H_{14}$-$C_{12}$-$H_{13}$) stretching vibration. On the lower side of spectra, two intense peaks due to scissoring modes of vibration, occur at 1612 $cm^{-1}$ and 1460 $cm^{-1}$. A very intense polarized peak occurs at 1472 $cm^{-1}$ with polarization vector directed along bond $C_{17}$-$H_{21}$ due to S($H_{14}$-$C_{12}$-$H_{13}$)adj$R_2$. At higher frequency region an intense polarized peak at 3760 $cm^{-1}$ with polarization vector directed along $N_{15}$-$C_{16}$ due to μ ($O_{27}$-$H_{28}$) $R_2$ occurs. From lower side of IR spectra two intense peaks occur at 709 $cm^{-1}$,713 $cm^{-1}$ due γ ($O_{27}$-$H_{28}$) $R_2$. The O-H group present in our molecule is expected to be most sensitive which shows noticeable shifts in the spectra of the hydrogen-bonded species.

***NBO analysis***

Natural bond orbital analysis is used to study interaction among the bond and charge transfer or

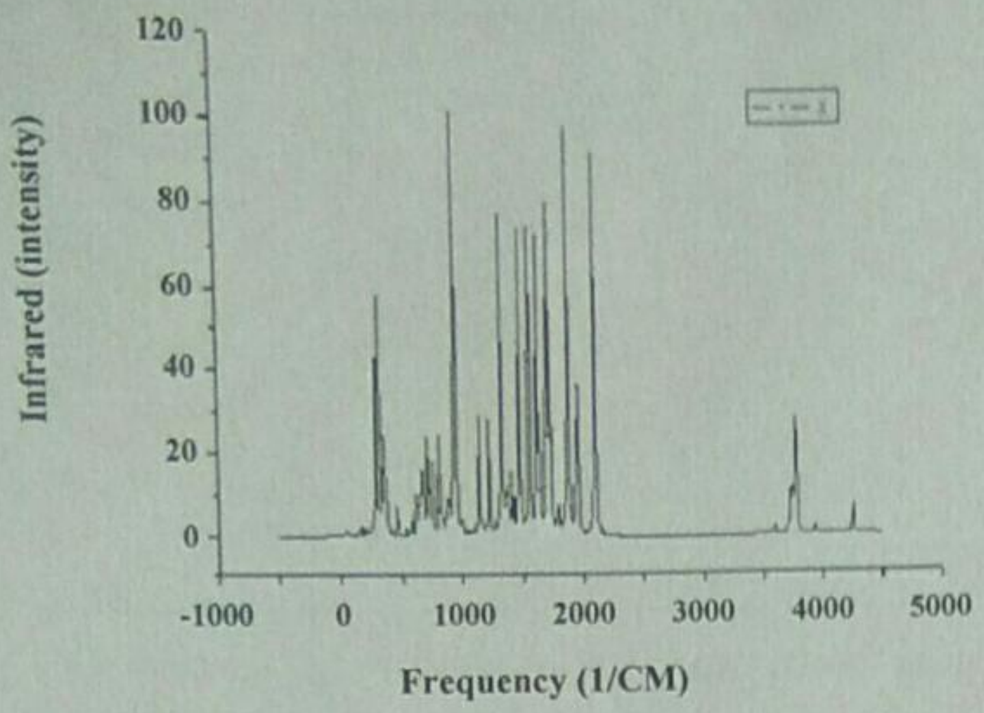


***Fig. 7: Calculated IR spectra of Title molecule using combination of DFT/B3LYP method and 6-311G(d, p) basis set.***

conjugative interactions in a molecular system. NBO analysis provides information about how electron density gets transferred from the bonding orbitals to the antibonding orbitals [39]. The strength of these interactions depends on the value of the second order energy of interaction between the donor and acceptor orbitals. The interaction between electron donors and electron acceptors is intense If the value of $E^{(2)}$ is high. The second order energy lowering is calculated by using each donor NBO(*i*) and acceptor NBO(*j*) and the strength of delocalization interaction [40]

$$E^{(2)} = -q_i \frac{F_{ij}}{\varepsilon_j - \varepsilon_i}$$

Several significant interactions are listed for the study molecule in Supplementary Table 4. From this table this is clear that σ electron density (1.976e - 1.983e) shows higher value than π electron density (1.862e -1.665e). In this molecule mainly σ → σ* π→ σ*,π→π* ,LP→π*/ σ* interactions occurs between bonding antibonding orbitals i.e. The σ → σ * interactions between bonding and antibonding orbitals are found to be σ (C23-C25)→σ* (C22-O26) and σ (C16-C18)→σ* (C18-C21), having $E^{(2)}$ values of 10.04 kcal/mol and 4.15 kcal/mol respectively. The π→ σ * interactions between bonding and antibonding orbitals which stabilized molecule is found to be π (C2-C3)→σ*(C4-C5) with $E^{(2)}$ 45.21 kcal/mol. The π→ π* interactions between bonding and antibonding orbitals are π (C1-C6) →π* (C2-C3), π (C1-C6)→π* (C4-C5),π (C4-C5) → π* (C2-C3), π (C4-C5) → π* (C1-C6), having $E^{(2)}$ values 46.69 kcal/mol, 46.75 kcal/mol, 48.01 kcal/mol and 45.21 kcal/mol respectively. The strongest interaction LP→ π*/ σ* involving lone pairs and nearly vacant antibonding orbitals such as LP(1) N15→π* (C16-C18)and LP(1) N22→π* (C17-C20) and LP(2)O26→σ* (C22-N23) have high $E^{(2)}$ values of 67.11 kcal/mol 72.42 kcal/mol and 24.69 kcal/mol respectively. These interactions contribute the greatest role to stabilizing the molecule.

*Biological activity and docking*

PASS [41] predicts Methylenetetrahydrofolate reductase to be inhibitor (0.7610) and having Antiallergic biological activity (0.7180), which is based on the structure activity relationships with Pa > 0.70. In methyl cycle Methylene tetrahydrofolate, reductase is the rate-limiting enzyme .The molecule under study inhibits this enzyme and prevent the human body from Alzheimer, other forms of dementia, colon cancer and acute leukemia disease. The molecule shows better activity against allergic diseases which are caused by hypersensitivity of the immune system typically harmless substances in the environment [42]. Swiss dock [43] is online webserver, which predicts suitable binding protein for the molecule is 5P4Q [44]. The structure 5P4Q has in total one chain with sequence from Cryphonectria parasite. The Cryphonectria parasitica is fungus belonging to Ascomycota taxon pathogen. It is the main cause of chestnut disease, a shocking disease of the American chestnut trees. [45]

After predicting suitable protein we perform docking of the molecule with the trial protein 5P4Q by Swiss Dock web server. All the probable conformers of the ligand and their corresponding energy values are resolute and best binding modes are ranked allowing to the full fitness (FF). This docking process is not covered on specific region of the chosen protein but blind follows whole region of chosen protein. The highest negative values of full fitness score shows best binding site between protein and the taken molecule. The full fitness score obtained in docking is -1051.65 A.U. Docking between title molecule and 5P4Q protein is shown in Fig. 8 using UCSF chimera software. The binding sites between title molecule and 5P4Q protein are H9and LIG (residue) and distance between H9-LIG is 2.169$A^0$. . FF score and docking between title molecule and 5P4Q protein shows

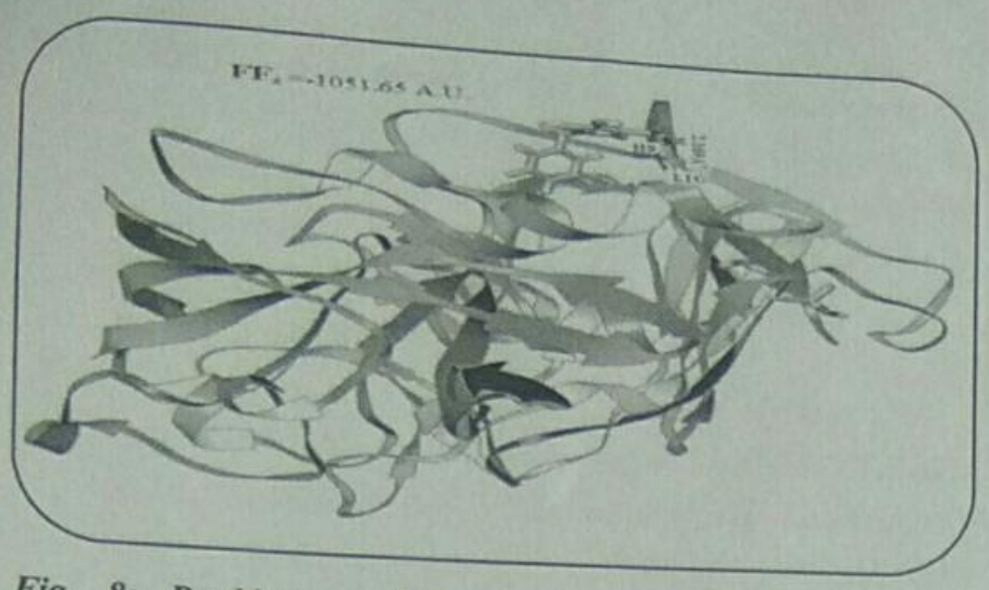


***Fig. 8: Docking of Title molecule with 5P4Q protein predicated by Swiss Dock wave server.***

that the molecule can be useful to stop fungus related dieseses. This study gives a pathway for drug researcher to design new drugs for fungus related diseases.

## CONCLUSIONS

In this paper we calculate geometric parameters, vibrational frequencies, electronic and the non-linear optical properties of title molecule using combination of DFT/B3LYP method and 6-311G (d, p) basis set. Optimized geometry clearly shows that the molecule is non-planar. Correlation factor > 0.99 between calculated and experimental value shows that they are well matched with each other. Non-linear optical behavior of the molecule shows that title molecule is optically active along the plane of the molecule. The molecular electrostatic potential contours and surfaces show that electron density transfer to benzene ring. NBO analysis shows that strongest interaction between bonding and antibonding orbitals is LP (1) N22 $\rightarrow\pi^*$ (C17-C20) with $E^{(2)}$ values 72.42 kcal/mol. The molecule shows better activity against allergic diseases.

*Received : Aug. 7, 2018 ; Accepted : Nov. 5, 2018*

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Reg. No. : 600/2009-10 ISSN 0975 – 7880

# MANAVIKI

An International Peer Reviewed and Refereed Research Journal of
Humanities & Social Sciences

UGC List No-: 42515 IIJF Impact Factor-: 3.097

Vol. XII No. I Issue-2 JANUARY-JUNE 2020


A REFEREED JOURNAL OF THE SOCIETY FOR
EDUCATION & SOCIAL WELFARE, VARANASI – 221005
(INDIA)

Published by
Society for Education & Social Welfare
Varanasi – 221005
INDIA

IN ASSOCIATION WITH
K.R. PUBLISHERS AND DISTRIBUTORS
Baba Shopping Complex, Lanka, Varanasi –05

ISSN 0975-7880

JUNE 2020


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The Editors, Manaviki
Department of A.I.H.C. & Archaeology
Faculty of Arts, Banaras Hindu University
E-mail: manavikiresearchjournal@gmail.com
Mob. 09415682014, 9621429385

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# CONTENTS



Kuntal Kishor

# Health Amenities in Sitamarhi Municipality

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**Abstract:**

*Health amenities are one of the most important basic needs of modern human civilization. It has been proved through various studies in developed and developing countries that health facilities not only insures better health of the resident population but also drops fertility rate and enhance economic growth. In this research article author has found out the condition of health amenities in Sitamarhi Municipality with etic and emic approach. The first approach of the study is based on the data of available health amenities in the study area and second approach of the study is based on score of satisfaction of urban dwellers in the Municipality. Etic study of health amenities in Sitamarhi Municipality suggest that the health facilities in the town are average and need to be improved. On the other hand emic study of heath amenities in the study area suggest that population of the study area is well satisfied with the health amenities they get. Conclusively it can be said that the town is inhabited mostly by first or second generation migrants, who do not get these facilities in their village. So, they are satisfied with poor health facilities in the town.*

***Key words:*** *Amenities, fertility rate, economic development, etic, emic, migrants*

## Introduction: Health Amenities

Medical revolution in western world and diffusion of their innovative medical technologies in third world countries has gradually changed the health condition of world population. Mortality rate has substantially reduced after medical revolution and fertility rate is decreasing fast even in developing countries. **R. P. Mishra (1969)** writes "Poor health makes the people less productive. Less production means less income which in turns means increased poverty". So medical revolution in 1960s not only made people healthy but also wealthy. Better health facility in any region/ country ensures high economic development and vice versa. Welfare governments have different policies for development of health facilities for the population. Ayushman Bharat yojana (25 September, 2018) of Indian Government is world's largest health insurance scheme. India spends 1 percent of GDP for health facilities. (Times of India, New Delhi, 20 June 2018).

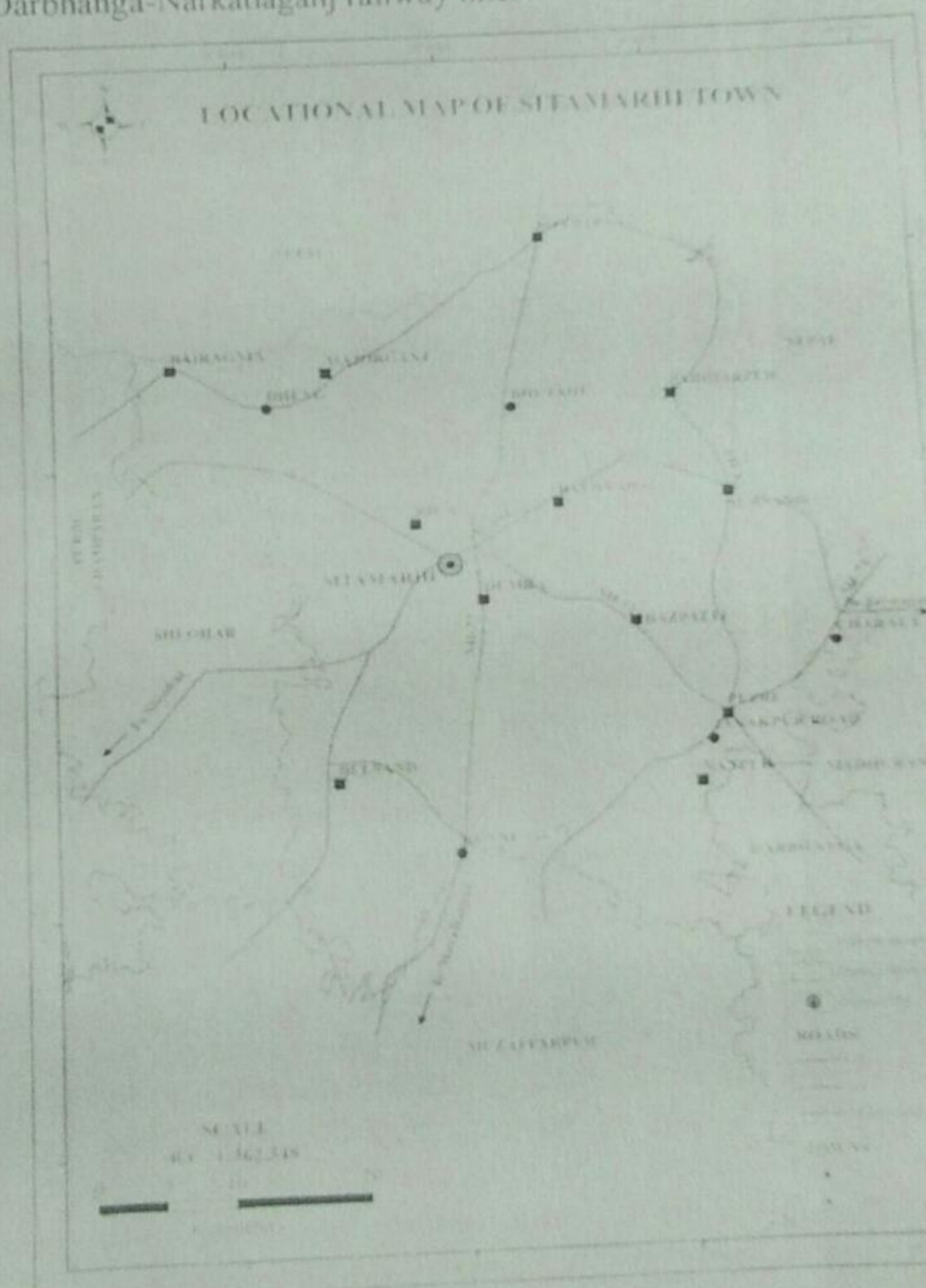
Health facilities include Hospitals and clinics, Drug manufacturing units and distribution outlets, drug research and development centers and health education. At the public end Hospitals and medical clinics, and drug outlets are the basic health amenities. State and Central Government together with Urban Local Bodies (ULBs) are equally responsible for provision and distribution of amenities in municipalities.

## Study Area: Sitamarhi Municipality

Sitamarhi Municipality is situated in Northern Ganga Plain geographical region. It is a small town of Bihar. The town Sitamarhi is administrative unit (municipal council) of Dumra block and situated in the center of the block. National Highway 77 connects it to Muzaffarpur and Patna district to the South. State highways link it to Madhubani district in the east and Sheohar district in the west. The town Sitamarhi is situated on the Darbhanga-Narkatiaganj railway line and has the largest railway station

of the district. There is another broad gauge track, running between Muzaffarpur and Sitamarhi. Sitamarhi municipality was constructed in 1882 and had a municipal board consisting of 12 commissioners. At that time there were only 4 wards in the town **(Bihar District Gazetteers Muzaffarpur, 1958)**. Now the municipality is divided into 28 wards. As a sequel to the great earthquake in 1934 district court was shifted to Dumara (in 1936) located at 5 km south of Sitamarhi town. Dumara Notified Town Area Committee was constituted in 1937. Sitamarhi urban agglomeration occupies Dumara Notified Town Area as a statutory town. At present most of the government offices of Sitamarhi district are situated in Dumara.

The study area, Sitamarhi municipal council is situated almost in the center of Sitamarhi district, within Dumara block and occupies an area of about 5 square kilometer. The shape of Sitamarhi municipal council (SMC) is almost rectangular. The SMC has maximum east-west extension of 4.5 km and maximum north-south extension of 3 km. The site of the town Sitamarhi is a flood free site on natural levee of river Lakhandei. The municipal council has rivarian situation on both side of the river Lakhandei and has an important location at the confluence of state highway and NH 77, and along Darbhanga-Narkatiaganj railway line.



**Research Problem:**

Research problem is an interrogative statement about relationship between different variables in the study area. To examine the condition of health amenities in Sitamarhi Municipality, researcher has formulated following research problems:

1. Is there any spatial variation in provision of health amenities?
2. Are the urbanites satisfied with the health amenities provided to them?

This research paper tries to find out the relationships; between geographical location and provision of health amenities, between provision of health amenities and degree of satisfaction of urbanites.

**Objective:**

Objectives of this study are:

1. To assess the condition of health amenities in different wards of Sitamarhi Town.
2. To find out spatial variation in provision of health amenities in the town.
3. To find out the degree of satisfaction of urbanites with health services.

**Methodology:**

The *etic* approach to find out the condition of health amenities in the study area includes collection of data regarding available health services in the town. For this purpose primary data from the town and secondary data of census survey (2011) have been collected by the investigator. *The emic* approach to find out condition of health amenities in Sitamarhi Municipality incorporates the assessment of satisfaction of urbanites with the health amenities provided to them. During execution of this research the investigator has collected primary data from twenty respondents from each wards of the town. This data represent the score of satisfaction with health amenities. Respondents were asked to give the score (1 to 5) to the health facilities they get in the town. Total score of satisfaction with different amenities in different wards of Sitamarhi Municipality has been calculated by adding individual score of satisfaction. On the basis of these composite scores of satisfaction with various amenities in every ward of the town, overall condition of urban amenities in Sitamarhi town and spatial variation in provision of urban amenities has been assessed.

Limitation of Methodology: This study is based on the data regarding level of satisfaction of the respondents. The satisfaction level of the respondent depends on their background (mental construct). People who have come from rural background are more satisfied with the facilities they get but on the other hand people with urban background feel these services in poor condition. So, this study is highly variable with people's background. In spite of this limitation this method is the most suitable way to study urban amenities, because people's appreciation is the most important factor for a service to become an amenity.

**Findings: Medical Amenities**

Sitamarhi town was frequently attached by epidemics like Cholera, Malaria and Chicken Pox before 1970s but the progress in sanitation and sewerage facility and better medical facilities has substantially reduced these microbial epidemics. The town has one Hospital at district level (Zila Aspatal) known as Sadar Hospital, Sitamarhi near Ramkrishna Goenka College. There is one PHC in Dumra, nearly 5 km from the main town where people from southern and Southwestern part of the town go for medical treatment. These two government Medical Centers are assisted by numerous private clinics and hospitals.

Table 1
**Health facilities in government hospitals, Sitamarhi (M), 2016**

| Hospital | Facilities | Quantitative/Qualitative Information |
|---|---|---|
| Sitamarhi Sadar Hospital | Number of Bed | 80 (available)<br>500 (sanctioned) |
| | Number of Doctors | 13 (sanctioned)<br>13 (available) |
| | Number of Nursing Staff | 29 (sanctioned)<br>29 (available) |
| | Number of other Staff | 6 |
| | Available Test Facilities | TLC, DLC, FNAC, Lipid Profile, Semen, Urine, Biopsy, BUN, Blood Sugar, SGPT, Culture, SGOG, X-ray, Ultrasound |
| | Departments | General Medicine, Surgery, Orthopedics, Gynaecology, Pediatrics, ENT, Dentistry, Diabetese ART, Dermatology, ANC Tuberculosis |
| PHC, Dumara | Number of Bed | NA |
| | Number of Doctors | 3 (sanctioned<br>2 (available) |
| | Number of Nursing Staff | 26 (sanctioned<br>26 (available) |
| | Number of other staff | 4 |
| | Available test facility | TLC, DLC, Lipid profile, Semen, Urine Blood Sugar, SGPT, Culture, X-ray, Ultrasound |
| | Departments | General Medicine, Surgery, Malaria, Tuberculosis, Gynecology |
| | Ambulance | 1 |

Source: District census handbook, Sitamarhi, series-11, part B, 2011

Several other functions like Immunization Camp, blood collection camp, Blood Sugar test Camp etc. are organized by Sadar hospital and Dumara PHC. These camps are very productive and task oriented having more than expected success rate. The town has many Private Hospital and clinics. Some of these are listed in tables above. Almost all facilities related to health and immunization is available in these hospitals.

Table 2
**Private Hospitals in Sitamarhi town (2016)**

| Name of Hospital | Number of bed |
|---|---|
| Ashirwad Hospital | 25 |
| Nandipant Hospital | 15 |
| Renu Singh Clinic | 75 |
| Dr. Anju Singh Hospital | 40 |
| Dr. Lata Gupta Hospital | 30 |

| | |
|---|---|
| Hospital Gunja | 25 |
| S.P. Jha Hospital | 20 |
| Suresh Bawesh Clinic | 25 |
| Sukhsagar Hospital | 25 |

Source: Information collected through field survey (2015-16)

Table 3

Composite score of satisfaction with medical facility in Sitamarhi(M)

| Ward Number | Total respondent | Score given by respondents (out of 5) | | | | | | Total score |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 4 | 3 | 2 | 1 | 0 | |
| 1 | 20 | 3 | 9 | 7 | 1 | 0 | 0 | 74 |
| 2 | 20 | 3 | 8 | 6 | 2 | 1 | 0 | 70 |
| 3 | 20 | 4 | 8 | 6 | 2 | 0 | 0 | 74 |
| 4 | 20 | 3 | 9 | 7 | 1 | 0 | 0 | 74 |
| 5 | 20 | 2 | 8 | 10 | 0 | 0 | 0 | 72 |
| 6 | 20 | 4 | 8 | 8 | 0 | 0 | 0 | 76 |
| 7 | 20 | 3 | 9 | 8 | 0 | 0 | 0 | 75 |
| 8 | 20 | 5 | 10 | 4 | 1 | 0 | 0 | 79 |
| 9 | 20 | 2 | 9 | 8 | 1 | 0 | 0 | 72 |
| 10 | 20 | 5 | 10 | 5 | 0 | 0 | 0 | 80 |
| 11 | 20 | 4 | 8 | 6 | 2 | 0 | 0 | 74 |
| 12 | 20 | 2 | 8 | 9 | 1 | 0 | 0 | 71 |
| 13 | 20 | 3 | 8 | 8 | 1 | 0 | 0 | 73 |
| 14 | 20 | 3 | 7 | 8 | 2 | 0 | 0 | 71 |
| 15 | 20 | 2 | 9 | 8 | 1 | 0 | 0 | 72 |
| 16 | 20 | 4 | 10 | 6 | 0 | 0 | 0 | 78 |
| 17 | 20 | 6 | 11 | 3 | 0 | 0 | 0 | 83 |
| 18 | 20 | 5 | 10 | 5 | 0 | 0 | 0 | 80 |
| 19 | 20 | 6 | 10 | 4 | 0 | 0 | 0 | 82 |
| 20 | 20 | 4 | 9 | 7 | 0 | 0 | 0 | 77 |
| 21 | 20 | 3 | 8 | 8 | 1 | 0 | 0 | 73 |
| 22 | 20 | 3 | 9 | 7 | 1 | 0 | 0 | 74 |
| 23 | 20 | 5 | 11 | 4 | 0 | 0 | 0 | 81 |
| 24 | 20 | 2 | 8 | 6 | 4 | 0 | 0 | 68 |
| 25 | 20 | 2 | 7 | 10 | 1 | 0 | 0 | 70 |
| 26 | 20 | 2 | 8 | 9 | 1 | 0 | 0 | 71 |
| 27 | 20 | 4 | 10 | 4 | 2 | 0 | 0 | 76 |
| 28 | 20 | 7 | 11 | 2 | 0 | 0 | 0 | 85 |

Source: Field survey (2016)

The data related to degree of satisfaction with the medical facility in the town shows that population living in ward number 10,17,18,19 and 23 are more satisfied with the facility than residents of other wards. It means medical facility in these wards is more satisfactory than in other wards.

Kittal Kishor

## Conclusion:

Etic study of health amenities in Sitamarhi Municipality suggest that the health facilities in the town are average and need to be improved. On the other hand emic study of heath amenities in the study area suggest that population of the study area is well satisfied with the health amenities they get. Conclusively it can be said that the town is inhabited mostly by first or second generation migrants, who do not get these facilities in their village. So, they are satisfied with poor health facilities in the town.

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Egyptian Journal of Basic and Applied Sciences xxx (2018) xxx–xxx

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Egyptian Journal of Basic and Applied Sciences

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Full Length Article

# Structural, IR spectra NBO, TDDFT, AIM calculation, biological activity and docking property of [1,2,4]-triazolo[3,4-*b*][1,3,4] thiadiazole

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ARTICLE INFO

*Article history:*
Received 6 August 2018
Received in revised form 7 October 2018
Accepted 11 October 2018
Available online xxxx

*Keywords:*
QTAIM
DFT
TDDFT
HOMO
LUMO
MESP
UV
MBNL1
NBO

ABSTRACT

In this paper a complete quantum chemical study of [1,2,4]-triazolo [3,4-b][1,3,4] thiadiazole has been done with the combination of DFT/B3LYP method and 6-311G(d, p) basis set. The vibrational assignments are calculated with the help of PED. By using quantum theory of atoms in the molecule (QTAIM) we have calculated topological parameters at BCP point by which the nature of several intermolecular hydrogen bondings are studied. Electronic properties are calculated with the help of HOMO-LUMO plot. Chemical active sites of title molecule are described by FF, chemical hardness, chemical softness etc. UV spectra are calculated with the help of TDDFT using optimized parameters. NBO analysis gives idea about transfer of charge between bonding and antibonding electrons. Biological activity analysis suggests that the molecule can be used in anti- inflammatory drugs to explore new drugs. The molecule is docked with MBNL1 receptor with the help of Swiss-Dock online server with Full fitness score of −541.58 a.u.


## 1. Introduction

1,3-thiazole containing both Nitrogen and sulphur is a heterocyclic compound. The term 'thiazole' refers to a large family of derivatives [1]. Thiazole having molecular formula $C_3H_3NS$ is a soft yellow liquid with pyridine-like scent [2] and used in a variety of specialized products, often by fusing with benzene derivatives. These are naturally occurring peptides, and utilized in the commercial development of peptidomimetics [3,4]. Thiazole is heterocyclic series organic compound characterized by a ring structure composed of three carbon atoms, one nitrogen atom, and one sulphur atom. This ring structure attributes many significant biologically active natural qualities such as thiamine, penicillin, and in many synthetic drugs, dyes, and industrial chemicals [5,6]. These are found in a number of various food products and flavors and are used in the manufacturing of prepackaged food products including noodles [7]. Thiazoles help flavorists to create healthier crops by enhancing the flavor of meats and savory foods without the accumulation of excess salts or fats [8]. 1,2,4-Triazole derivatives and their bonded heterocyclic correspondents are well known for their different biological activities and 1,2,4-triazole rings have been combined into ligands used in coordination compounds. The 1,2,4-triazole derivatives and their *N* bridged heterocyclic equivalents have been widely studied [9–14]. Numerous 3,6-disubstituted [1,2,4] triazole [3,4-*b*] [1,3,4] thiadiazoles are testified to display significant antibacterial [15–18], pesticidal [19], anticancerous [20], anti-inflammatory, and anti-oxidant activities [21]. Many studies are carried to synthesize organic compounds, inorganic metal complexes and are detected by using NMR FTIR spectra [22–27]. Monirah A. Al-Alshaikh etal. synthesized the crystal structure of [1,2,4]-triazolo[3,4-b][1,3,4] thiadiazole molecule and found it as a potential bioactive agent [22–28]. The present study on the [1,2,4]-triazolo[3,4-b][1,3,4] thiadiazole molecule has been carried out to support and as an extension of the work of Monirah A. Al-Alshaikh et al. [29]. As mentioned in the work of Monirah A. Al-Alshaikh et al., due to bioactive potential of the molecule its biological properties are studied by using several parameters and also docking is made for designing new anti-inflammatory drugs. Along with this the geometrical parameters, NMA, Biological and Chemical activities, electronic transitions,

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https://doi.org/10.1016/j.ejbas.2018.10.001
2314-808X/

Please cite this article in press as: Pandey AK et al. Structural, IR spectra NBO, TDDFT, AIM calculation, biological activity and docking property of [1,2,4]-triazolo[3,4-*b*][1,3,4] thiadiazole. Egyp. Jour. Bas. App. Sci. (2018), https://doi.org/10.1016/j.ejbas.2018.10.001

thermodynamic properties are studied by the combination of DFT/B3LYP method and 6-311G(d, p). A complete DFT analysis is performed on the title molecule (Fig. 1).

## 2. Computational details

All the calculations are done with G03 program package [29] using combination of B3LYP/DFT method and 6-311G (d, p) basis set. This basis set 6-311G (d, p), with 'p' polarization functions on hydrogen atoms and 'd' polarization functions on heavy atoms, is used for better description of polar bonds of molecule [30,31]. Initial geometry is modeled with the help of Gauss View 3.0 program package [32]. AIM calculation, performed by AIMALL program package [33], is based on quantum theory of atoms in a molecule. Natural bond analysis is carried with NBO 3.0 program package [34]. Electronic transitions, vertical excitation energies, and oscillator strengths are computed with the TD-DFT method.

## 3. Result and discussion

### 3.1. Optimized parameters

The molecule taken has two benzene rings, one thiazole and other phenyl rings. The molecule shows some deviation from planarity, with fluoro ring (C19-C14) forming dihedral angle of 2.65° and the phenyl ring (C12-N17) 3.84°. The distance of the interaction between benzene ring and thiazole ring C14-C19 is 2.33 Å.

AIM [35] calculation shows that there are two interactions between N18-H8 and N18-F29 in the molecule, which are shown in Fig. 2. According to Koch and Popelier standard, an existence of hydrogen bond follows bond critical point (BCP) for the 'proton (H)...acceptor (A)', [36] which involves electron density (q) in the range of 0.002–0.040 a.u. and Laplacian ($\nabla^2_\rho$) in the of range 0.024–0.139 a.u. All calculated parameters at BCP, in between N18-H8, and N18-F29, are listed in Table 1. On the basis of topological parameters three types of H-bonds are characterized. According to Rendering to Rozas et al. [37], the characterization demands, at BCP, that for strong and covalent nature of H-bond $\nabla^2_\rho < 0$ and $H < 0$, for medium and partially covalent nature of H-bond $\nabla^2_\rho > 0$ and $H < 0$, and for weak H-bond of electrostatic character $\nabla^2_\rho > 0$ and $H > 0$. From Table 1, the Laplacian of charge density are positive, however value of $H < 0$ signifies that the interaction is medium strong in nature. According to Espinosa et al. interaction energy calculated is $E_{int} = ½ V$ at BCP [38]. In this study calculated interaction energy of N18-H8, N18-F9 is 3.95 kcal/mol and 5.648 kcal/mol respectively.

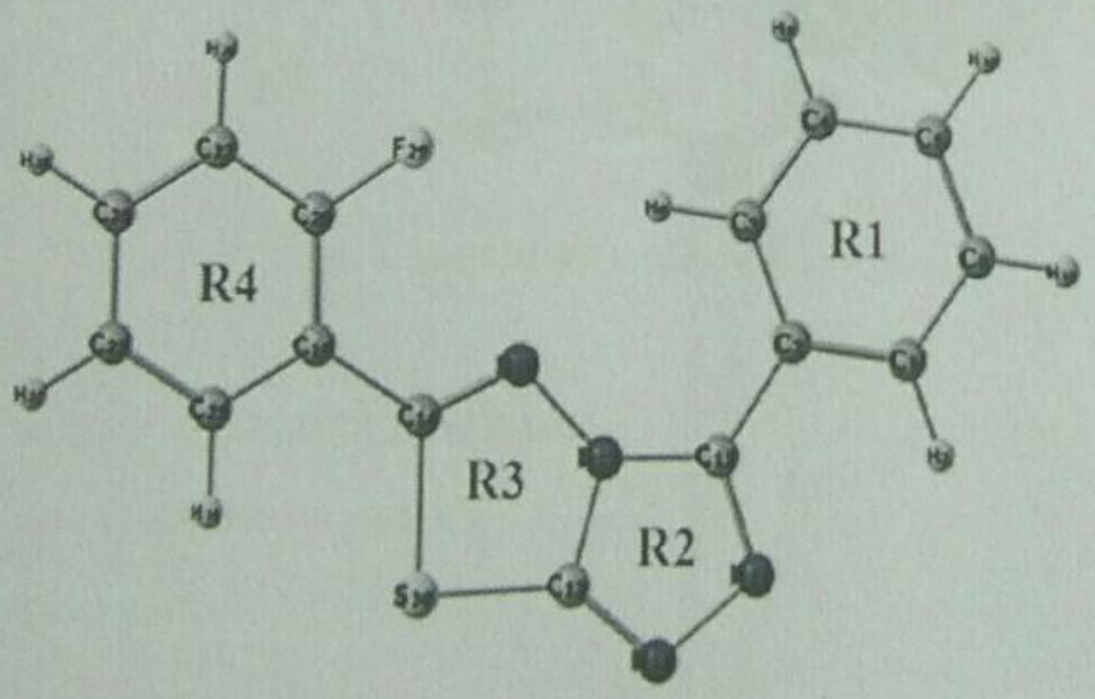


**Fig 1.** Molecular Picture of title molecule according to numbering.

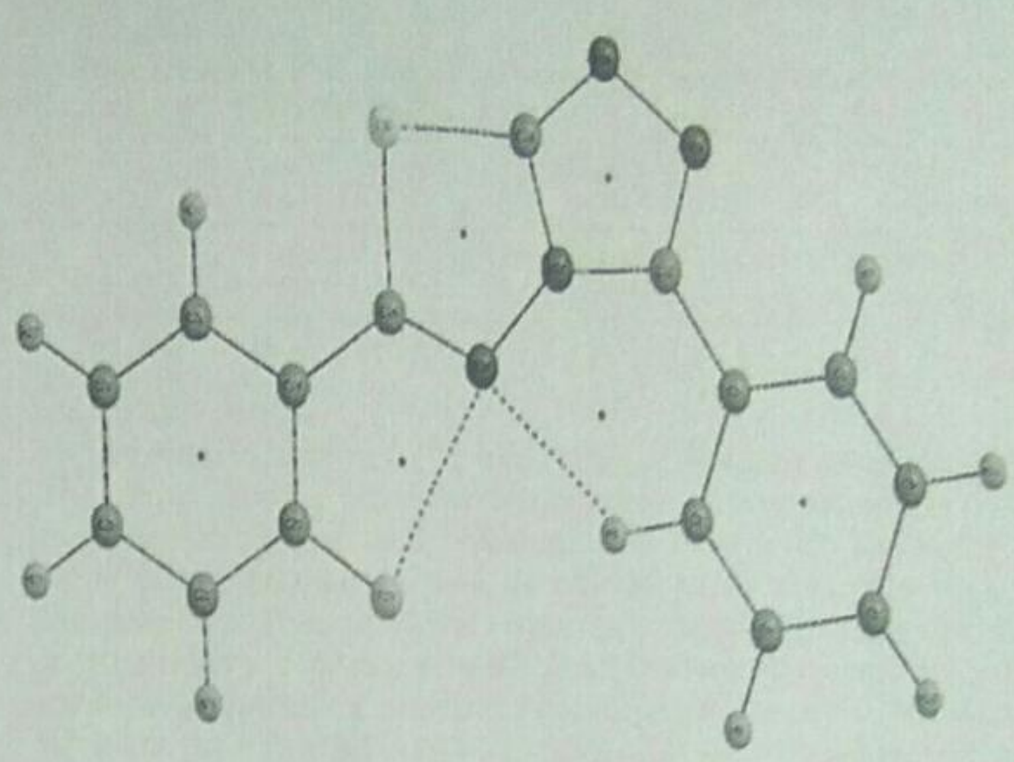

**Fig 2.** Molecular Graph of the studied compound at BCP.

### 3.2. Electronic property and HOMO-LUMO surfaces

The HOMO represents the ability to donate an electron by an atom while LUMO represents the ability to accept. The HOMO and LUMO energies are calculated by DFT/B3LYP method. The electronic parameters, such as highest occupied molecular orbital (HOMO) energy (E-HOMO), lowest unoccupied molecular orbital (LUMO) energy (E-LUMO) and band gap energy ($\Delta E$ = FLUMO-FHOMO) are described theoretically [39]. The energy ($E_{gap}$) between HOMO and LUMO in the present study is found to be 3.71 eV. In this molecule LUMO is located over whole molecule however HOMO is located only on benzene ring. The transition from HOMO → LUMO in the molecule indicates charge transfer from benzene ring to thiazole ring. The molecular electrostatic potential (MESP) is a map of potential i.e. electrostatic potential over constant electron density of all molecules. It displays molecular size and shape as well as positive, negative, and neutral electrostatic potential regions in terms of color grading scheme. In this color grading schemes, the blue color represents the most electropositivity i.e. low electron region, whereas the red color corresponds to the most electronegative center or electron rich regions [40,41].The MESP plot of title molecule is display in Fig. 3. From this fig. ring $R_2$ is covered by red region so it is the most electronegative region of title molecule. On the basis of energy of frontier orbitals, εHOMO, εLUMO [energy of highest occupied molecular orbital, Energy of lowest unoccupied molecular orbital respectively] the different global reactivity descriptors such as electronegativity $\chi$ (tendency to attract electrons), chemical potential $\mu$ (energy that can be absorbed or released), global hardness $\eta$ (hardness basically signifies the resistance against the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical response), global electrophilicity index $\omega$ (capacity of a species to accept arbitrary number of electrons) and global softness S (Softness signify how easily a molecule becomes polarized) are computed using equations as given below [42] (Fig. 4).

The energies of frontier molecular orbitals (εHOMO, εLUMO), energy band gap (εLUMO–εHOMO), electronegativity ($\chi$), chemical potential ($\mu$), global hardness ($\eta$), global softness (S), and global electrophilicity index ($\omega$) of the molecule have been listed in Table 2. On the basis of εHOMO and εLUMO, these parameters are calculated by using equation given below [43–45]

$$\chi = -1/2(\varepsilon LUMO + \varepsilon HOMO)$$

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**Table 1**
Topological parameters for bonds of interacting atoms: electron density ($\rho$BCP), Laplacian of electron density ($\nabla^2$BCP), kinetic electron energy density (G BCP), potential electron energy density (VBCP), total electron energy density (HBCP), estimated interaction energy ($E_{int}$) at bond critical point (BCP).

| O–H | $\rho_{BCP}$ (a.u.) | $\nabla^2\rho_{BCP}$ (a.u.) | $G_{BCP}$ (a.u.) | $V_{BCP}$ (a.u.) | $H_{BCP}$ (a.u.) | Eint (kcal/mol) |
|---|---|---|---|---|---|---|
| N18-H8 | 0.0150 | 0.0630 | 0.0142 | −0.013 | −0.014 | 3.953 |
| N18-F29 | 0.0159 | 0.0897 | 0.0201 | −0.018 | −0.0186 | 5.648 |

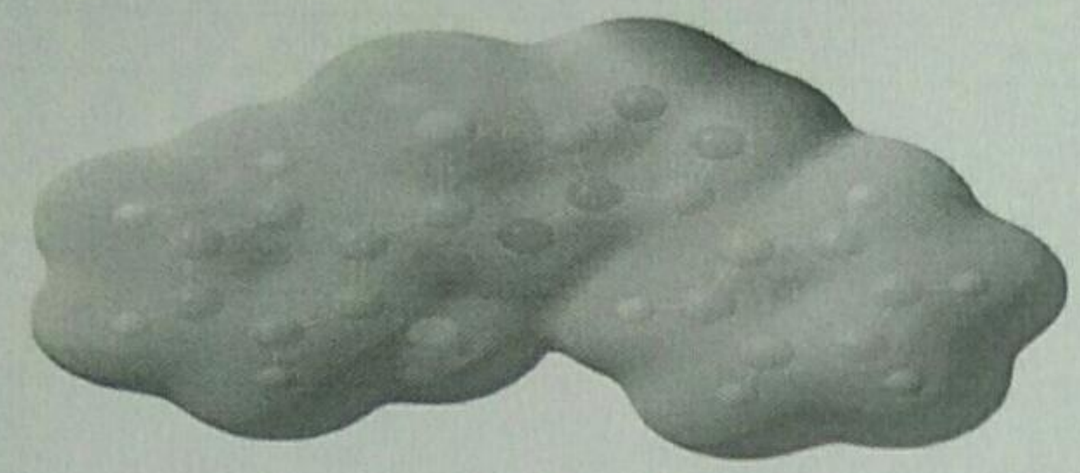

**Fig. 3.** MESP surfaces of thiazol.

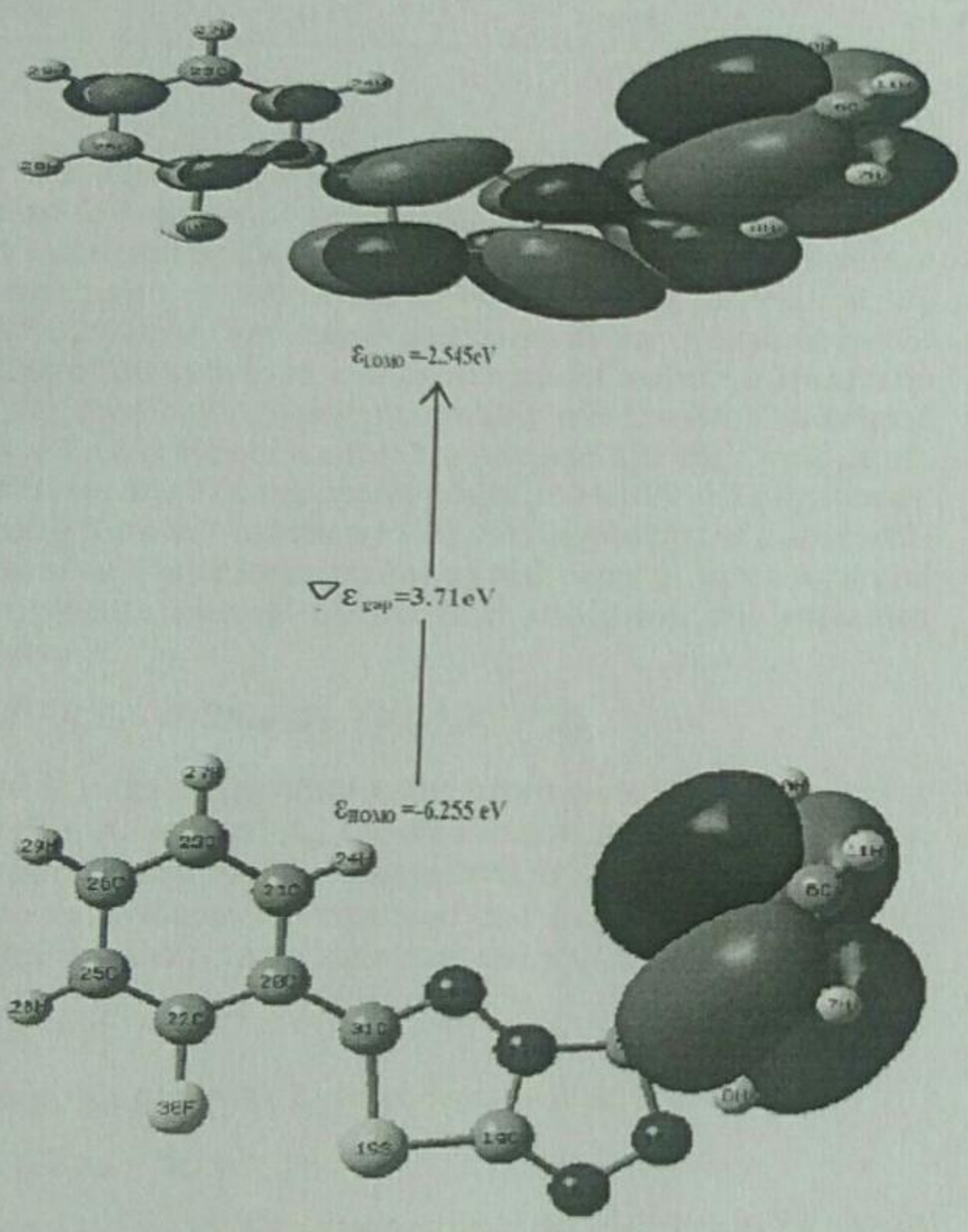


**Fig. 4.** HOMO, LUMO surfaces of thiazol.

$$\mu = -\chi = 1/2(\varepsilon LUMO + \varepsilon HOMO)$$

$$\eta = 1/2(\varepsilon LUMO - \varepsilon HOMO)$$

$$S = 1/2\eta$$

$$\omega = \mu^2/2\eta$$

*3.2.1. Fukui function*

The Fukui function (FF) [46,47] of a molecule provides information about reactive sites and the method of understanding as well as categorizing chemical reactions. The atom with the highest FF value is highly reactive site as compared to the other atoms in the molecule. The use of the Fukui functions for the site selectivity in title molecule for nucleophilic and electrophilic attacks has been made with special emphasis on the dependence of the Fukui values with the basis of B3LYP/6-311G(d, p) level of theory. Using the Mullikan atomic charges of neutral, cation, and anion, state of the molecule, the Fukui functions ($f_k^+$, $f_k^-$, $f_k^0$), local softness ($S_k^+$, $S_k^-$, $S_k^0$) [48] and local electrophilicity indices ($\omega_k^+$, $\omega_k^-$, $\omega_k^0$) are calculated using the following equations

$$f_k^+ = [q_k(N+1) - q_k(N)] \text{ for nucleophilic attack}$$

$$f_k^- = [q_k(N) - q_k(N-1)] \text{ for electrophilic attack}$$

$$f_k^0 = 1/2[q_k(N+1) + q_k(N-1)] \text{ for radical attack.}$$

where $q_k$ is electronic population of atom k in the neutral molecule with N electrons.

Local softness and electrophilicity indices are calculated using

$$S_k^{\pm} = Sf_k^{\pm}, \quad S_k^o = Sf_k^o, \quad \omega_k^{\pm} = \omega f_k^{\pm}, \quad \omega_k^o = \omega f_k^o$$

where +, −, and 0 signs show nucleophilics, electrophilics, and radical attacks, respectively. The Fukui functions, for all the carbon atoms in both benzene ring ($R_1$ $R_4$) and sulfar atom in thiazole ring ($R_3$), calculated by using combination of DFT/B3LYP method and 6-311G (d, p) basis set are listed in Table 3. From Table 3, it can be seen that the carbon of both benzene ring, 14C and 31C are more reactive sites for nucleophilic and 26C as an electrophilic reactive attacks. However 30S atom of the thiazole ring shows more favorable site for both electrophilic and nucleophilic substitution than ring carbon atoms. Furthermore, 30S site is more reactive to the electrophilic than nucleophilic substitution because $f_k^- > f_k^+$.

Time dependent density functional theory (TD–DFT) method is important tool for studying the nature of the transitions of UV–vis spectrum of the compound. Optimized geometry is obtained for TD-DFT calculation by using same level theory. UV spectra of the molecule, calculated by combination of DFT/B3LYP method and 6-311G (d, p) basis set is shown in Fig. 6. In this graph, two prominent peaks observed at 4.02 eV (294 nm), 2.03 eV (610 nm) originate mainly due to H → L (37%), H-4 → L (43%) transitions respectively. These transitions are shown in Fig. 5 and listed in Table 4. On the basis of the calculated molecular orbital coefficients analyses electronic transition are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively.

*3.3. Non linear optical parameter*

The Gaussian 03 program is used to calculate the dipole moment ($\mu$) and polarizability ($\alpha$) of the molecules, based on the finite field approach. The first hyperpolarizability ($\beta$) and polarizibility of the title molecule are calculated by using same level the-

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**Table 2**
Electronic parameters of title compound calculated by DFT/B3LYP method and 6-311G(d, p).

| HOMO energy | LUMO energy | Electronegativity ($\chi$) | Chemical potential ($\mu$) | Global hardness ($\eta$) | Global softness (S) | Global electrophilicity index ($\omega$) |
|---|---|---|---|---|---|---|
| −6.255 | −2.545 | 4.400 | −4.400 | 1.855 | 0.270 | 5.218 |

**Table 3**
Fukui values on the basis theory of the Mulliken atomic charges of neutral, cation, and anion, the Fukui functions ($f_k^+, f_k^-, f_k^0$).

| S.N | Neutral | Positive | Negative | $f_k^+$ | $f_k^-$ | $f_k^0$ |
|---|---|---|---|---|---|---|
| 1C | −0.133 | −0.128 | −0.136 | 0.005 | 0.003 | −0.132 |
| 2C | −0.171 | −0.173 | −0.163 | −0.002 | −0.008 | −0.168 |
| 3C | 0.188 | 0.190 | 0.191 | 0.002 | −0.003 | 0.191 |
| 4C | −0.171 | −0.169 | −0.169 | 0.002 | −0.002 | −0.169 |
| 5C | −0.133 | −0.129 | −0.135 | 0.004 | 0.002 | −0.132 |
| 6C | −0.123 | −0.113 | −0.129 | 0.010 | 0.006 | −0.121 |
| 12C | 0.041 | −0.011 | 0.077 | −0.052 | −0.036 | 0.033 |
| 14C | 0.313 | 0.344 | 0.239 | 0.031 | 0.074 | 0.292 |
| 20C | 0.069 | 0.063 | 0.070 | −0.006 | −0.001 | 0.066 |
| 21C | −0.160 | −0.147 | −0.183 | 0.013 | 0.023 | −0.165 |
| 22C | 0.313 | 0.332 | 0.285 | 0.019 | 0.028 | 0.309 |
| 23C | −0.132 | −0.126 | −0.134 | 0.006 | 0.002 | −0.130 |
| 25C | −0.190 | −0.181 | −0.199 | 0.009 | 0.009 | −0.190 |
| 26C | −0.124 | −0.105 | −0.154 | 0.019 | 0.030 | −0.130 |
| 31C | 0.039 | 0.065 | 0.002 | 0.026 | 0.037 | 0.034 |
| 30S | 0.301 | 0.484 | 0.118 | 0.183 | 0.183 | 0.301 |

ory and listed in Table 5. In the presence of applied electric field, energy is function of applied electric field. Hyperpolarizability and Polarizability are described as the response of a system due to application of the electric field [49]. The Hyperpolarizability and Polarizability are determined by nonlinear optical properties (N L O) of the system as well as strength of molecular interaction [50,51]. First order Hyperpolarizability of the system is defined by 3 × 3 × 3 matrix of is a third rank tensor. The third rank matrix which contains 27 components can be reduced to 10 components by using Kleinman symmetry [52]. All components of $\beta$ are coefficients in the Taylor series expansion of the energy. When weak and homogeneous external electric field is applied, this expansion becomes

$$E = E^0 - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta}F_\alpha F_\beta - 1/6\beta_\alpha\beta_\gamma F_\alpha F_\beta F_\gamma$$

where $E^0$ is the energy of the unperturbed molecules, $F_\alpha$ the field at the origin $\mu_\alpha$, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta}$ are the components of dipole moment, polarizability and the first hyperpolarizabilities respectively.

The total dipole moment and the mean polarizability and hyperpolarizability using x,y,z components are defined as

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

where $\mu_x$, $\mu_y$, $\mu_z$ are X,Y,Z components of dipole moment

$$\langle\alpha\rangle = 1/3[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$$

where $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$ are the components of polarizibility in XX, YY, ZZ planes

$$\beta_{Total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$
$$= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

where $\beta_{abc}$ are components of hyperpolarizibility along a direction and in bc plane and (1 a.u. = 3.6998 × $10^{-30}$ e.s.u.).

The calculated value of dipole moment is 6.29 D. In title molecule $\alpha_{xx}$ and $\alpha_{yy}$ have greater contribution of polarizibility which indicates that the molecule is more polarized along Y and X directions. The calculated value of hyperpolarizibily of given molecule is nearly same as, 2-{[5-(adamantan-1-yl)-4-methyl-4H-1,2,4-triazol-3-yl]sulfanyl}-N,N-dimethylethanamine [53], and nearly one fifth of Thiazole Azo Dyes.[54] Urea is benchmark compound for NLO properties, therefore we compare our results with urea. The calculated value of hyperpolarizibily of the compound is nearly nine times greater than hyperpolarizibily of urea so it is a good claimant as a NLO material.

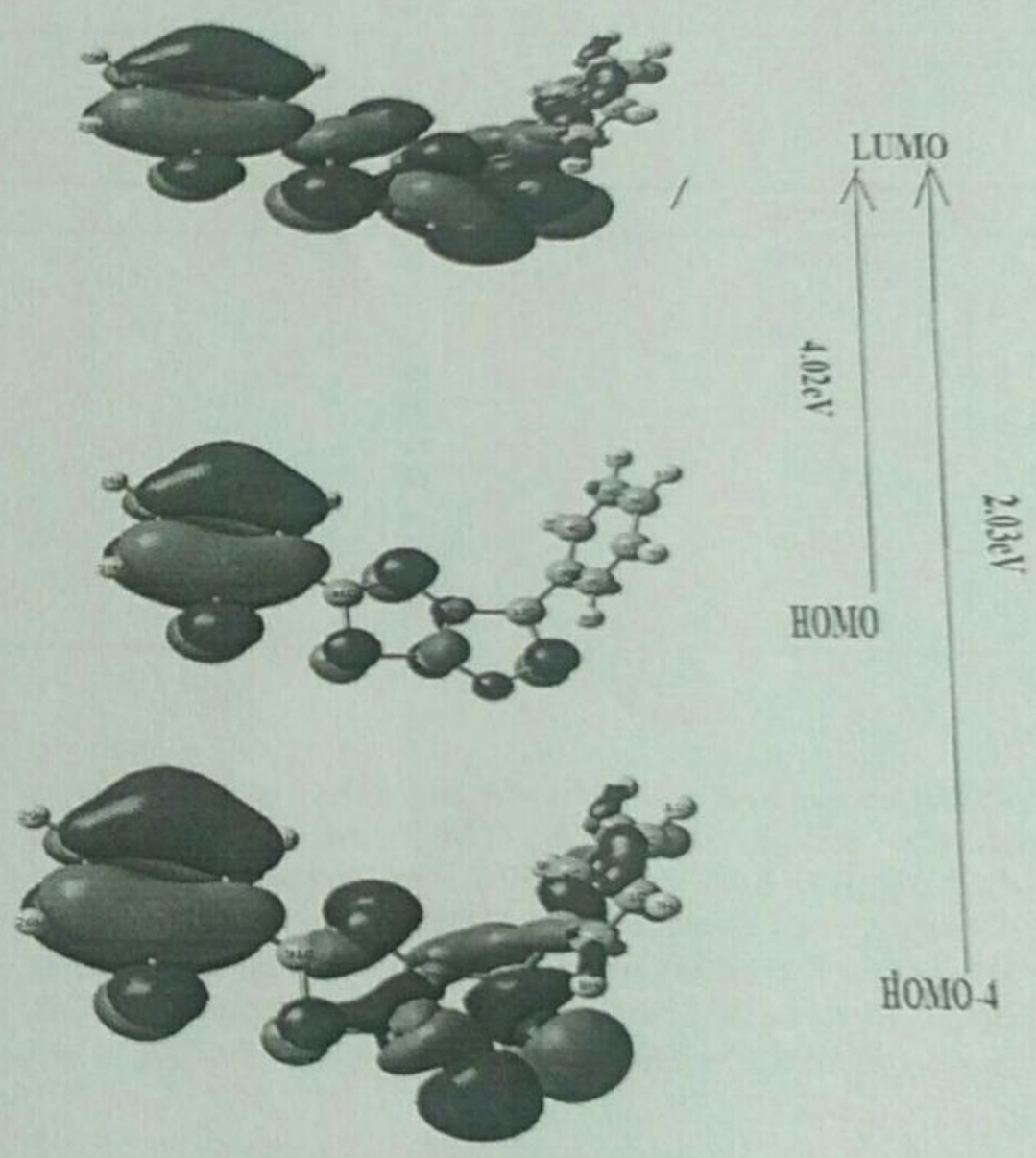


**Fig 5.** Electronic Transition of TD-DFT of title molecule by DFT/B3LYP method.

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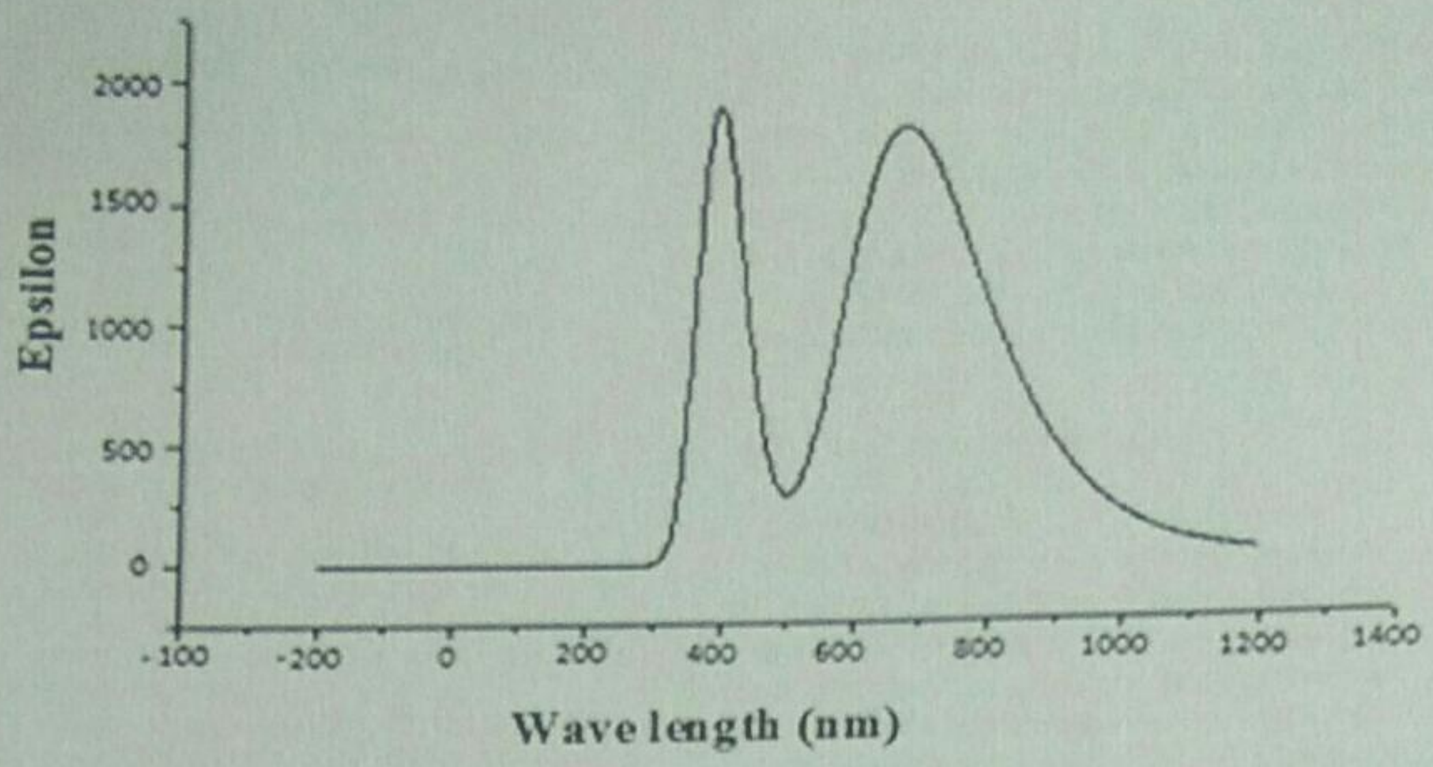


**Fig 6.** UV spectra of title molecule calculated by combination of DFT/B3LYP method and 6-311G(d,p) basis set.

**Table 4**
The observed UV–vis spectra as calculated by TD-DFT method at B3LYP/6-311 G (d, p) level.

| Excitation energy (eV) | Wavelength (nm) | | Oscillator strength | Orbital transition |
|---|---|---|---|---|
| | Calculated | Assignment | | |
| 4.02 | 294 | $n \rightarrow \pi^*$ | 0.023 | HOMO → LUMO (43%) |
| 2.03 | 610 | $\pi \rightarrow \pi^*$ | 0.130 | HOMO-4 → LUMO (37%) |

**Table 5**
Polarizability and Hyper Polarizability of title compound calculated by same level theory.

| S.N. | Parameter | Polarizability | S.N. | Parameter | Hyper Polarizability |
|---|---|---|---|---|---|
| 1. | $\alpha_{xx}$ | −113.889 | 1. | $\beta_{xxx}$ | −130.786 |
| 2. | $\alpha_{yy}$ | −129.426 | 2. | $\beta_{yyy}$ | 58.531 |
| 3. | $\alpha_{zz}$ | 0.393 | 3. | $\beta_{zzz}$ | 4.053 |
| 4. | $\alpha_{xy}$ | 6.624 | 4. | $\beta_{xyy}$ | −42.254 |
| 5. | $\alpha_{xz}$ | 2.339 | 5. | $\beta_{xxy}$ | 77.013 |
| 6. | $\alpha_{yz}$ | −2.853 | 6. | $\beta_{xxz}$ | 35.379 |
| 7 | $\alpha$ | −9.678 | 7. | $\beta_{xzz}$ | 14.626 |
| | | | 8. | $\beta_{yzz}$ | −1.132 |
| | | | 9. | $\beta_{yyz}$ | −1.432 |
| | | | 10. | $\beta_{xyz}$ | −1.856 |
| | | | 11. | $\beta$ | 211.201 |

### 3.4. Vibrational analysis

The molecule under study contains 30 atoms, so there are 3N-6 modes of vibrations. All mode of vibration are studied with the help of combination of Gauss View and VEDA 4.0 program package [55]. In our calculations we ignore electron- electron correlation as well as an-harmonicity [56,57]. These approximations cause calculated frequencies to be in higher region than experimental results, therefore we scale calculated frequency by 0.9688. [58] Some of selected modes of vibrations are listed in Table 6 and calculated IR spectra of the molecule is also plotted in Fig. 7, using same level theory. Some important modes of vibrations are discussed below.

#### 3.4.1. C-H stretching

The hetero aromatic structure shows the presence of C–H stretching vibrations in the region 2800–3100 $cm^{-1}$ [58]. In the present study the C–H stretching vibration of the title compound is observed at 3066–3108 $cm^{-1}$. Two sharp back to back peaks observed at 3077 $cm^{-1}$, 3076 $cm^{-1}$ due to $\upsilon$(C-H)$R_1$ and mixing of $\upsilon$(C-H)$R_1$,$R_4$ with PED 24%, 43% respectively, are well matched with experimental as well as calculated IR spectra of 2-(4-methoxyphenyl)benzo[d]thiazole at 3076 $cm^{-1}$ [59]. An intense mixing of modes are observed at 1625 $cm^{-1}$ due to $\beta$ (CH) $R_1$ with PED 16%. In mid region of spectra very intense and sharp polarized peaks are observed at 1611 $cm^{-1}$ and 1605 $cm^{-1}$ due to $\beta$ (CH)$R_1$, $\beta$(CH)$R_4$ respectively with PED 47% and 76%. In lower region some out of plane bending and twisting mode of vibrations occur.

#### 3.4.2. C-N vibrations

The determination of C-N vibrations is a difficult task, because of the mixing of vibration in this region. Silverstein [58] has first time assigned C-N stretching absorption in the range of 1382–1266 $cm^{-1}$. The C-N stretching vibration (15N-12C) and (17N-12C) in the molecule observed at 1266 $cm^{-1}$ and 1263 $cm^{-1}$ with PED contribution 15% and 46% respectively, are well matched (1267 $cm^{-1}$) with C-N stretching mode and lies in the same region as 2-(4-methoxyphenyl)benzo[d]thiazole [59]. In lower rage of frequency some other in plane bending vibration modes (14C-18N-17N) and torsion (14C-18N-17N-12C) are obtained at 1088 $cm^{-1}$ and 654 $cm^{-1}$ respectively with PED contribution 20% and 79%.

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**Table 6**
Theoretical (selected) vibrational wave numbers of title molecule using B3LYP/6-311G (d, p) and their assignment.

| Cal. Freq. | Sc. freq | IR Int. | Mode of vibration |
|---|---|---|---|
| 3176 | 3077 | 22.26 | R1[υ (1C-7H) (24%)] |
| 3175 | 3076 | 4.35 | R1[υ (6C-11H) (24%)] |
| 3172 | 3073 | 33.69 | R4[υ (26C-29H)] (27%) + R1[υ (1C-7H)] (16%)] |
| 3168 | 3069 | 4.36 | R1[υ (4C-9H) (47%) + υ (5C-10H) (26%)] |
| 3154 | 3056 | 3.89 | R4[υ (25C-28H) (50%)] |
| 3152 | 3054 | 3.89 | R1[υ (1C-7H) (49%)] |
| 3148 | 3050 | 9.39 | R4[υ (21C-24H) (37%)] + R1[υ (6C-11H) (26%)] |
| 1677 | 1625 | 540.56 | R1[β (2C-3C) (11%)] + R1[β (1C-2C) (14%)] |
| 1663 | 1611 | 581.20 | R1[υ (2C-3C) (47%)] |
| 1657 | 1605 | 34.93 | R4[ β (24H-21C)(42%)] + R4[β (22H-23C) (34%)] |
| 1637 | 1586 | 40.23 | R1[υ (1C-2C)[31%)] + R2[υ (15 N-12C) (11%)] |
| 1622 | 1571 | 52.34 | R1[υ (1C–2C) (29%)] + R1[β (6C-11H)(34%)] |
| 1577 | 1528 | 14.89 | R1[υ (5C-4C) (14%)] + R1[β (5C-4C-6C) (15%)] |
| 1540 | 1492 | 19.68 | R1[β (1C-2C-3C) (14%)] |
| 1520 | 1473 | 14.30 | R1[β (8H-2C) (17%)] + R4[β (21C-23C-26C) (21%)] |
| 1493 | 1446 | 0.12 | R1[β (10H-5C-6C) (11%)] + R1[β (8H-2C-1C) (13%)] |
| 1477 | 1431 | 150.32 | R1[υ (1C-2C) (27%)] |
| 1411 | 1367 | 29.25 | R3[υ (14C-30S) (17%)] |
| 1408 | 1364 | 34.13 | R1[υ (2C-3C) (15%)] + R1[β (8H-2C-1C) (21%)] |
| 1383 | 1340 | 2.43 | R1[γ (3C-2C-1C) (21%)] |
| 1341 | 1299 | 9.29 | R2[υ (14C-18N) (19%)] + R2[υ (15 N-12C) (13%)] |
| 1327 | 1286 | 3.30 | R2[υ (12C-17N) (27%)] + R1[ β(3C-6C-5C) (15%)] |
| 1326 | 1285 | 3.24 | R2[υ(15N-12C) (39%)] |
| 1287 | 1247 | 10.02 | R2[ β(17N-12C-15N) (14%)] + R3[β(18N-14C-30S) (23%)] |
| 1254 | 1215 | 150.36 | R1[ υ(2C-3C) (18%)] + R2[β(12C-15N-16N) (13%)] |
| 1218 | 1180 | 15.79 | R2[ υ(17N-14C) (21%)] + R3[γ(14C-18N-17N) (19%)] |
| 1187 | 1150 | 64.61 | R3[υ(14C-30S) (17%)] + R1[γ(11H-6C-5C) (23%)] |
| 1176 | 1139 | 0.26 | R2[β(17N-12C-15N) (23%)] + R3[ β(17N-14C-18N) (21%)] |
| 1150 | 1114 | 15.86 | R4[ γ(26C-23C-21C) (15%)] + R1[ γ (1C-2C-3C) (21%)] |
| 1119 | 1084 | 5.45 | R2[υ(15N-12C) (13%)] + R4[β(22C-29F) (42%)] |
| 1107 | 1072 | 0.73 | R3[ β(18N-14C-30S) (46%)] + R1[ β(3C-2C-1C) (15%)] |
| 1002 | 971 | 0.45 | R2[β(17N-12C-15N) (12%)] + R1[β(1C-2C-3C) (11%)] |
| 976 | 946 | 5.62 | R3[υ(30C-18N) (15%)] |
| 966 | 936 | 6.31 | R4[τ(20C-21C-22C-23C) (24%)] + R3[τ(14C-17N-18N-30S) (21%)] |
| 925 | 896 | 30.44 | R2[υ (15N-12C) (22%)] |
| 865 | 838 | 0.71 | R4[τ(22C-23C-25C-26C) (11%)]+R2[τ(17N-12C-15N-16N) (10%)] |
| 850 | 822 | 1.05 | R2[β(14C-17N-18N) (13%)] |
| 776 | 752 | 10.88 | R1[ τ(3C-6C-1C-2C) (11%)] + R3[τ(14C-17N-18N-30S) (15%)] |
| 660 | 639 | 5.24 | R1[γ(6C-5C-4C) (11%)] + R2[γ(12C-15N-16N) (17%)] |
| 655 | 635 | 6.47 | R1[τ(3C-6C-2C-1C) (24%)] + R3[τ(14C-18N-17N-13C) (18%)] |
| 606 | 587 | 0.98 | R4[γ(19C-20C-22C) (17%)] + R1[γ(1C-2C-3C) (13%)] |
| 531 | 514 | 279.57 | R3[τ(13C-17N-18N-30S) (30%)] + R1[τ(6C-5C-4C-3C) (42%)] |

*Abbreviations:* β = in plane bending, γ = out of bending, ω = wagging, τ = twisting, S = scissoring, R = rocking, υ = stretching. Note: The PED distribution less than 12% are neglected for the sake of calculation.

### 3.4.3. C-C vibrations

Normally the (C-C) stretching vibrations are expected within the middle region of spectra. The C–C stretching vibrations of the aromatic compounds, calculated by B3LYP/6-311G (d, p) method, are at 1600 $cm^{-1}$, 1586 $cm^{-1}$, 1568 $cm^{-1}$, 1500 $cm^{-1}$ and 1293 $cm^{-1}$ in thiazole ring however in benzene ring C–C aromatic stretching mode of vibrations lies in between 1645 and 847 $cm^{-1}$. The other modes of vibration i.e. in-plane and out-of-plane bending are also observed at lower frequencies.

### 3.4.4. Other modes of vibration

Some other modes of vibrations are also reported at lower range of frequencies. In thiazole ring intense plane polarized mode of vibration due to υ (29F-20C) with PED 19% is obtained at 1207 $cm^{-1}$. In this study below 1000 $cm^{-1}$ half segment of thiazole ring experiences torsion τ (14C-17N-18N-30S) at 936 $cm^{-1}$ with PED 21%, however opposite half segment of thiazole ring experiences very intense peak of torsion τ (29F-19C-22C-20C) at 520 $cm^{-1}$ with PED 27%. In fuoro ring a medium intense polarized mode of vibration with polarization vector along the plane of ring, due to υ (29F-20C), is obtained at 1207 $cm^{-1}$ with PED 15%. Some other modes of vibrations are reported in table however those mode of vibration are not reported for which PED < 15%.

## 3.5. Donor acceptor interaction

### 3.5.1. NBO analysis

NBO gives the most suitable 'natural Lewis structure' because all orbitals include the highest possible percentage of the electron density (ED). NBOs deliver an accurate method for studying intra and intermolecular interaction as well as charge transfer or conjugative interaction in different molecular systems [60]. The value of $E^{(2)}$ shows the strength of interaction in between electron donors and electron acceptors, i.e., As the value of $E^{(2)}$ increases the strength of interaction increases and vice-versa. For each donor NBO($i$) and acceptor NBO($j$), the strength of delocalization interaction (or stabilization energy) $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated by the second order energy lowering as [61,62]

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_i - \varepsilon_j}$$

where $q_i$ is the population of donor orbital or donor orbital occupancy; $\varepsilon_i$, $\varepsilon_j$ are orbital energies (diagonal elements) of donor and acceptor NBO orbitals respectively; $F_{ij}$ is the off-diagonal Fock or Kohn–Sham matrix element between $i$ and $j$ NBO orbitals. The second-order perturbation analysis of Fock matrix in NBO basis are listed in Table 7. From this table we see that strong intramolecular hyper conjugative interactions are formed by orbital overlap Lp(1)N15/N17,Lp(2)S30,σ(C-C),σ(C-H)π(C-C)σ*(C-C), σ*(C-H), π*(C-C) which results in intra-molecular charge transfer causing stabilization of the system. From Table 7, interactions between C1-C2 to C3-C4, C5-C6 of π(C1-C2) → π*(C3-C4) and π(C1-C2) → π*(C3-C4) with electron density 0.9897 e stabilize by 10.28 kcal/mol, 10.49 kcal/mol respectively. The interaction between C3-C4 to C1-C2, C4-C5, C12-C17 of π(C3-C4) → π*(C1-C2) π(C3-C4 → π*(C5-C4), π(C3-C4) → σ*(C12-C17) with electron density 0.833e stabilizes by 10.04 kcal/mol, 9.72 kcal/mol and 3.11 kcal/mole respectively. Similarly interaction between C5-C6 to C3-C4, C1-C2, of π(C5-C6) → π*(C3-C4) π(C5-C6) → π*(C1-C2) with electron density 0.829 e stabilizes by 9.6 kcal/mol, 10.54 kcal/mol respectively. A strong interaction observed in between lone pair $L_P$(1)N17 → π*(C14-N18), π*(N18-C31) with energy 21.09 kcal/mol and 20.25 kcal/mol respectively are comparable with interaction has been observed due to the electron density transfer from the lone pair (LP1) of nitrogen atom to antibonding orbitals π*(C–N) and π*(N–C) with stabilization energies 41.07 and 46.78 kcal/mol, respectively in similar molecular system 2-{[5-(adamantan-1-yl)-4-methyl-4H-1,2,4-triazol-3-yl]sulfanyl}-N,N-dimethylethanamine [53]. Since π orbitals have lower occupancies than σ, correspondingly showing more electron- donating ability in comparison to σ orbital. This also shows that [$L_P$(1) (S30) → π*(C14-C16)] is the most intensive interaction between the acceptor and donor which results in the molecular stability. A very strong interaction by π* to π* orbital overlap of π*(C22-C25) → π*(C23-C26) stabilizes by 153.69 kcal/mol. In this system stabilization occurs by intermolecular interactions of orbital overlap among π and π* orbitals, which results in intermolecular charge transfer (ICT). Since ICT makes molecule more polarized, it must be responsible for the NLO

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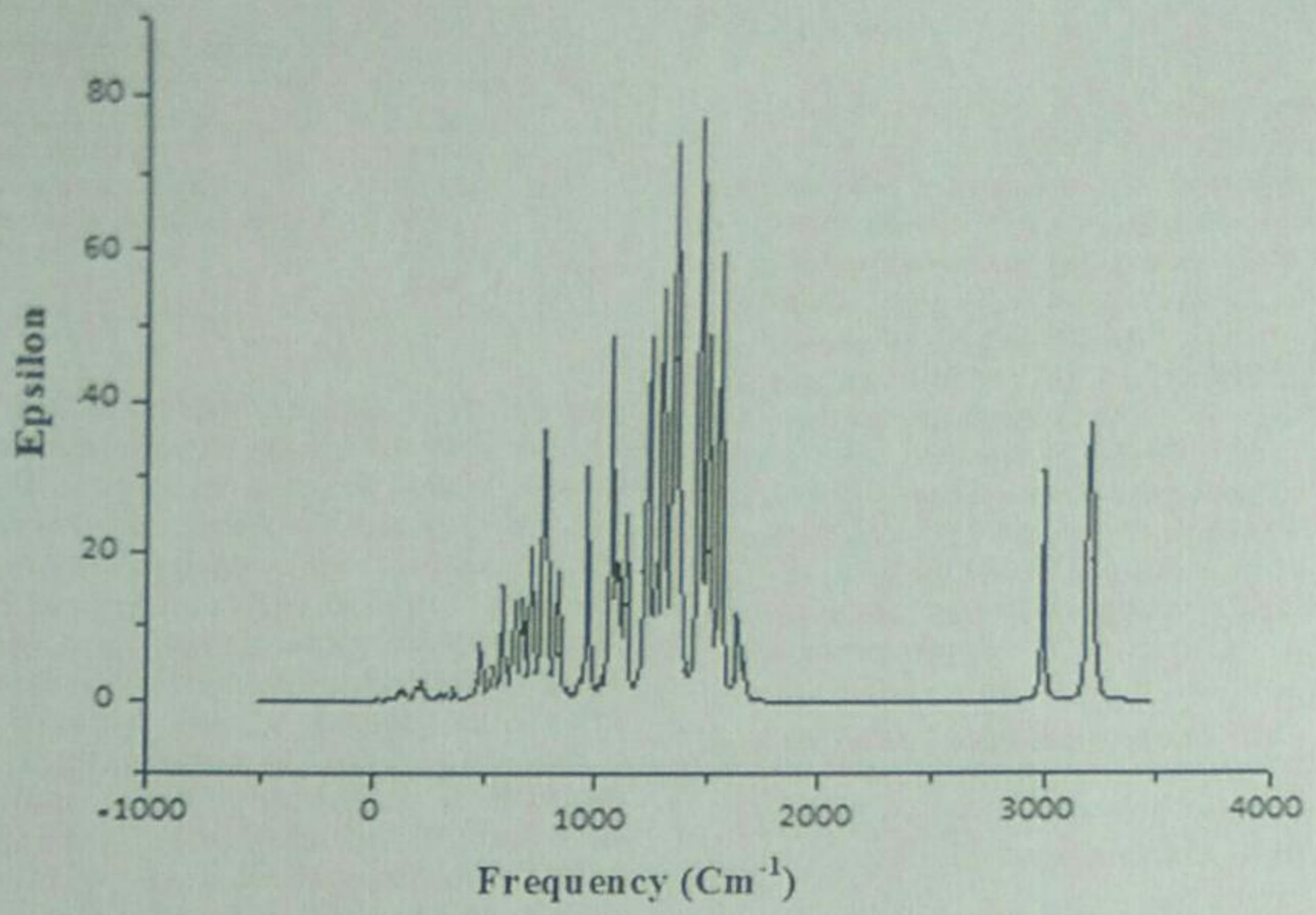


**Fig 7.** Calculated IR spectra of title molecule by using DFT/B3LYP method.

**Table 7**
Second–order perturbation theory analysis of the Fock matrix, in the NBO basis for intermolecular interactions within title molecule: Stabilization energy of interactions ($E(2)$), Energy difference between donor ($i$) and acceptor ($j$) NBO orbitals ($Ej–Ei$), Fock matrix element between $i$ and $j$ NBO orbitals ($Fij$).

| Donor NBO (*i*) | Occupancy (*i*) | Acceptor NBO (*j*) | Occupancy (*j*) | $E^{(2)}$ (kcal/mol | (*Ej–Ei*) a.u | *F*(*i*,*j*) a.u. |
|---|---|---|---|---|---|---|
| π (C1-C2) | 0.9897 | π*(C3-C4) | 0.1792 | 10.28 | 0.28 | 0.07 |
| π(C1-C2) | 0.9897 | π*(C5-C6) | 0.1632 | 10.49 | 0.28 | 0.07 |
| σ(C1-C6) | 0.9906 | σ*(C1-C2) | 0.0070 | 1.26 | 1.28 | 0.05 |
| σ(C1-H7) | 0.9914 | σ*(C2-C3) | 0.0118 | 1.88 | 1.10 | 0.06 |
| σ(C1-H7) | 0.99140 | σ*(C5-C6) | 0.0078 | 1.78 | 1.10 | 0.06 |
| π(C3-C4) | 0.8334 | π*(C1-C2) | 0.1552 | 10.04 | 0.29 | 0.07 |
| π(C3-C4) | 0.8334 | π*(C5-C6) | 0.1632 | 9.72 | 0.28 | 0.07 |
| π(C3-C4) | 0.8334 | σ*(C12-N17) | 0.0308 | 3.11 | 0.55 | 0.06 |
| π(C5-C6) | 0.8296 | π*(C1-C2) | 0.1552 | 9.60 | 0.28 | 0.07 |
| π(C5-C6) | 0.8296 | π*(C3-C4) | 0.1792 | 10.54 | 0.28 | 0.07 |
| Lp(2) N15 | 0.9998 | π*(C14-S30) | 0.0226 | 22.72 | 0.21 | 0.09 |
| Lp(1) N17 | 0.9996 | π*(C14-N18) | 0.2496 | 21.09 | 0.27 | 0.10 |
| Lp(1) N17 | 0.9996 | σ*(N18-C14) | 0.0337 | 20.25 | 0.26 | 0.09 |
| Lp(2)S30 | 0.9997 | π*(C14-N18) | 0.0138 | 11.85 | 0.25 | 0.07 |
| Lp(2)S30 | 0.9997 | π*(N18-C30) | 0.2145 | 9.85 | 0.25 | 0.06 |
| Lp(3)F29 | 0.9999 | π*(C22-C25) | 0.0135 | 9.34 | 0.43 | 0.09 |
| π*(N17-C13) | 0.1732 | π*(C12-C2) | 0.0245 | 28.45 | 0.04 | 0.07 |
| π*(C22-C25) | 0.1840 | π*(C23-C25) | 0.0165 | 153.69 | 0.01 | 0.08 |

properties of molecule. Consequently the compound may be used for NLO materials in future.

### 3.6. Biological properties

Before discussing the biological activity of the molecule aqueous solubility (log *S*) and Lipophilicity (log *P*) are calculated. For evaluating log *P* and log *S*, ALOGPS 2.1 program [63] is used. This program developed by Tetko et al. [64–66] is based on electrotopological state indices and associative neural network modeling. The Structure-property relationship studies are justified by these two parameters. The transport property of drugs and their interaction with receptors are closely related by Log *P* however bioavailability is closely related by log *S*. The calculated value of log *P* is 2.34 which suggests that molecule is able to diffuse across the cell membranes, so it can be utilized in pharmacological applications. In general 85% of drugs have log *S* values in between the range of −1 to −5.36. The calculated value of log *S* (−3.30) further approves the permeability of molecules through cell membranes. Some biological activities of title molecule are calculated with the help of PASS software. PASS calculates 900 pharmacological properties, molecular mechanisms of action, mutagenicity, carcinogenicity, teratogenicity, and embryotoxicity. PASS predicts these properties on the basis of structure activity relationships for the training set, considering more than 46 000 drugs, drug candidates, and prime compounds whose biological activity are resolute experimentally. The calculated results by PASS software have average accuracy of about 85% [67]. In this study we only listed those biological activities, in Table 8, for which Pa > 70%. The molecule shows high value of biological activity for Chloride peroxidase inhibitor. The Chloride peroxidase belongs to the family of enzymes, which catalyzes the chlorination of organic compounds. It employs one cofactor, which may be either heme or vanadium [68]. The molecule inhibits chlorination of organic compounds in blood stream which prevents

**Table 8**
Some biological activities calculated by PASS with Pa > 70%.

| S.N. | Biological activity | Pa | Pi |
|---|---|---|---|
| 1. | Chloride peroxidase inhibitor | 0.756 | 0.005 |
| 2. | Albendazolemonooxygenase inhibitor | 0.688 | 0.004 |
| 3. | Corticosteroid side-chain-isomerase inhibitor | 0.682 | 0.010 |
| 4. | Phobic disorders treatment | 0.686 | 0.082 |
| 5. | Glucocorticoids | 0.646 | 0.050 |

bacterial disease. It is used for Phobic disorders treatment also. Phobias are the most common type of anxiety disorder, in which a person experiences an extreme or irrational fear of a place, object, animal, or situation. Corticosteroid side-chain isomers exist in all organs but show highest activity in liver and kidneys. The molecule inhibits Corticosteroid side-chain isomers in liver and kidneys and protect these organ from multiple myeloma. Glucocorticoids (0.646) are part of the response mechanism in the immune system which decreases certain features of immune function, such as drop of inflammation [69]. So they are used as medicines to treat diseases caused by an intense resistant system. They also inhibit growth in cancer cells, therefore high doses of Glucocorticoids are used to treat cancer. This contains inhibitory effects on lymphocyte production, as in the handling of lymphomas and the moderation of side effects of anticancer drugs. Designing new anti-inflammatory in Myotonic dystrophy diseases, agents require the identification of targets, which when inhibited can kill the affected cells. We have done molecular docking studies by using Swiss-Dock web server [70]. MBNL1 receptor is identified as an efficient target, based on the prediction by Swiss-Dock web server. Muscleblind-like (Drosophila), also known as MBNL1, is a protein which is encoded in humans by the MBNL1 gene [71–73]. MBNL1 is stated in the early heart, and its levels rise across fatal and postpartum development. The docking score is expected to have minimum interaction energy value (e-value). As more negative the e-value is the docking becomes more efficient. Docking process does not cover on a specific region but over entire protein. The docking picture of the molecule, obtained from the UCSF chimera software, is shown in Fig. 8. The Full Fitness score for the title molecule is −541.58 a.u. and binding affinity (ΔG in kcal/mol) −5.46 a.u., which suggest that it has good binding affinity. The results obtained from docking studies suggest that the compound can be used as an anti-inflammatory agent in Myotonic dystrophy.

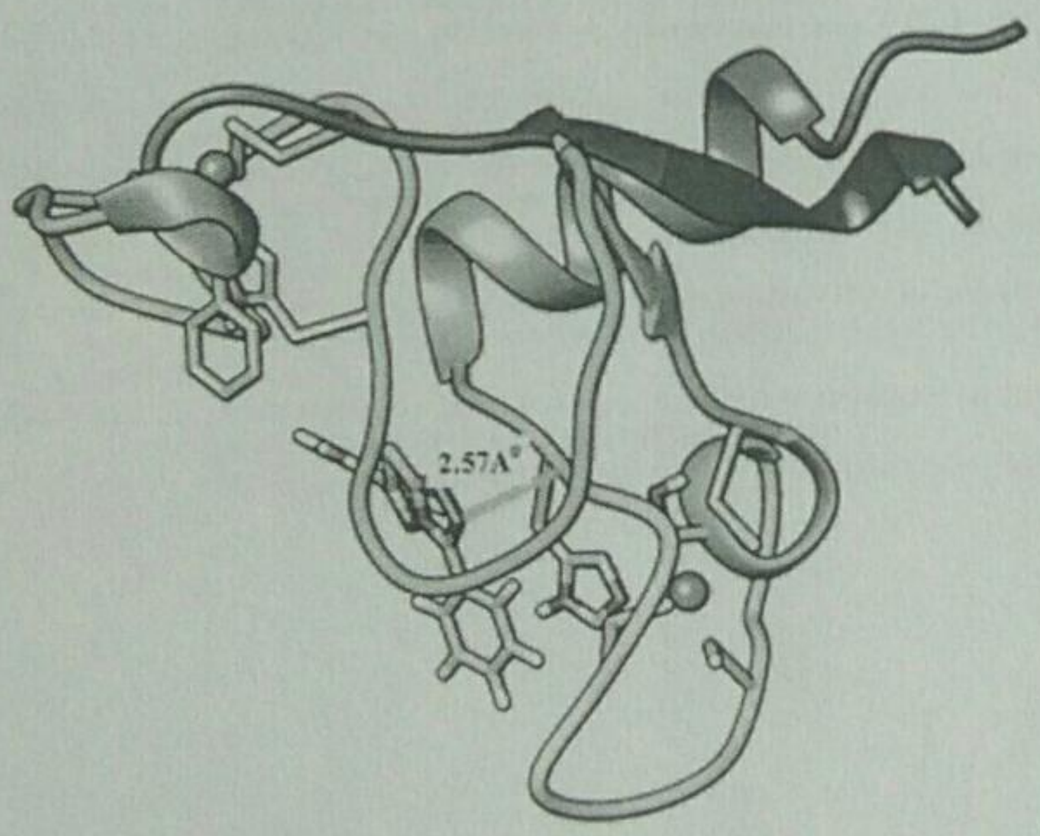


**Fig 8.** Molecular Docking of MBNL1 protein with title molecule.

## 4. Conclusion

Equilibrium geometries, harmonic frequencies, electronic properties, NBO, NLO analysis, TDDFT and biological activity of title molecule are determined and analyzed using combination of DFT/B3LYP level of theory using 6-311G (d, p) basis set. The theoretical calculation of UV–vis spectra shows a medium intense peak (at 610 nm) corresponding to H-4 → L. The NBO analysis shows that strongest interaction with energy 153.69 kcal/mol corresponding to $\pi^*$(C22-C25) → $\pi^*$(C23-C26) stabilizes flouro ring. The chemical reactivity of the molecule is explained by energy gap (3.71 eV) and plot of HOMO-LUMO. FF shows that 14C and 31C are better nucleophilic centers however 30S shows better electrophilic center. Full Fitness score corresponding to docking of the molecule with and MBNL1 protein is −541.58 a.u. The molecular docking of title molecule suggests that it can bind and inhibit the receptor enzymes.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ejbas.2018.10.001.

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PROBLEMS OF URBAN AMENITIES IN SMALL TOWNS: A case study of Sitamarhi Municipality

Vol. 10 Issue 8 No. 8 August 2020

Published in

JUNI KHYAT JOURNAL ISSN: 2278-4632

6.625

This journal is indexed, peer reviewed and
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Editor

6.625

Impact factor

Jnani Khyat
(UGC Care Group I Listed Journal)
ISSN: 2278-4632
Vol-10 Issue-8 No. 8 August 2020

# PROBLEMS OF URBAN AMENITIES IN SMALL TOWNS:
## A case study of Sitamarhi Municipality

**Dr. KUNTAL KISHOR**, Assistant Professor, Department of Geography, Government College Bishrampur, Affiliated to Sant Gahira Guru University, Surguja, Ambikapur, Chhattisgarh

**Abstract:**

Urban amenities are facilities, services and infrastructure provided to town dwellers for a better life. Provision and maintenance of urban amenities has been a challenge in small towns of India. Present study is a discourse over the problems of urban amenities in small towns in general and in Sitamarhi town in particular. Author has collected primary data through schedule and interview method during 2016-17 and secondary data from different government and non-government sources. These data have been analyzed with suitable methods and result has been processed at the end. Investigator found many structural and institutional problems in provision and maintenance of urban amenities in the study area. Similar problems have been found by the researcher in other small towns during review of literature. So it can be generalized that small towns in India face problems of urban amenities like poor quality and quantity of infrastructure, services and facilities and lack of civic sense in urbanites together with malfunctioning of institutions involved in provision and maintenance of urban amenities in small towns.

Methodology: present research work is based on the data and information regarding urban amenities in Sitamarhi town. For this study primary data and information has been collected from urbanites residing in Sitamarhi town through schedule and some data and information has been collected through personal interview of ward members and municipal officers. Some information for this study has been collected through empirical observation by researcher. Secondary data has been collected from census report of year 2011. Descriptive analysis of these data and information has been done to get results.

Result: descriptive analysis of data and information collected from the study area reveals that there are several structural and institutional problems of urban amenities in the study area. These problems are mainly associated with provision of urban amenities to the residents and implementation of government programmes for upliftment of the condition of urban amenities in the study area.

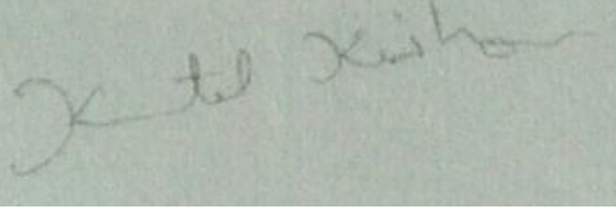
Conclusion: Small towns, with lesser fund and without managerial expertise, are not able to provide adequate urban facilities to its inhabitants. On the basis of analysis of data and information gathered from the study are it can be said that poor quality of services, inadequate services and facilities, lack of civic sense in urbanites together with malfunction of institutions involved in provision and maintenance of urban amenities are some of the problems found in small towns of India.

## INTRODUCTION

Government institutions in India may applaud for their synergy to make one third of Indian population urban but most of the towns, mainly small towns, in India have lesser amenities than rural settlements of United States. Census of India defines a census town as 'a settlement with more than 5000 population having density more than 400 person per square kilometer and where at least 75 % of male working population is engaged in non-agricultural activities'. This definition of town undermines the importance of availability of urban amenities in towns. Poor infrastructure and poor quality of public utility services is characteristic feature of small towns in India. Though some of these towns have more open space and urban green than big towns but







ISSN: 2278-4632
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quality of environment is poor due to impoverished drainage and sanitation facilities in small towns. Lack of public utility services and urban facilities is the only reason behind the fact that 70% of urban population in India live in medium or large towns and only 30% urban population of India lives in small towns of India. Other reasons behind this fact are just consequences of the previous one.

On the basis of population size towns in India can be categorized as; Small Towns having population less than one lakh (1, 00,000), Medium Towns having population one lakh or more but less than one million, Big Town having population more than one million. Out of 7935 towns in India only 465 towns have population one lakh or more. It means more than 94 % towns in India are small towns. About 30% urban population of India lives in these small towns other 70 % urban population is concentrated in 6% towns of India (Census survey, 2011). There is huge gap in population density of medium or large towns and small towns. This difference in concentration of population explains the variation in provision of urban amenities in small towns and big towns. Not only the size of population is low in small towns of India but the facilities, services and infrastructure are also poor here. Dr. Kuntal Kishor (2018) found that although most of the resident population in Sitamarhi town, a small town in Bihar province of India, is satisfied with the services and facilities they get but condition of these services and facilities is very poor and need to be improved as soon as possible.

**Small town as a center of economic development**

Small towns play important role in development of country in general and rural hinterland in particular. The symbiotic relationship between rural and urban settlement is clearly visible in around small towns (Cecilia Tacoli, 2017). Small town provide non-agricultural employment to rural population and add value to the agro products from rural areas through small food processing units in these small towns. For local small farmers these towns are affordable market and service centers. Small town receives raw material for food processing units and cheap laborer from rural hinterland. These small towns also provide educational, medical and recreational facilities to rural hinterland. Like other towns Sitamarhi town provide employment to rural hinterland. For the same hinterland Sitamarhi town is service center and market. The area of influence of Sitamarhi town, on the basis of method adopted by V.L.S. Prakash Rao, is a circular 65 $km^2$ area having radius of about 4.5 kilometers

**Small town as a safety valve for big cities**

Small towns reduce pressure of population in big cities in India. It can be further improved by development of small towns. The resource and population ratio is decreasing day by day in big cities of India due to large scale flow of immigrants from small towns and rural areas. Further, high density of population, traffic congestion, slum development, increase in crime rate and many other problems are related with huge rate of immigration in big towns. Increase in population of big towns of India adds to the burden of local governing bodies for provision of services and facilities in limited resources. As a consequence quality of public utility services and urban facilities have deteriorated in these towns. Development of small towns could attract more immigrants from rural area and check emigration from small towns and condition in big cities could also improve in this way. So these small towns are safety valve for big cities from where big city can release pressure of population. Small towns can be improved to a center of excellence in provision of services, employment and education through investment in secondary and tertiary sectors.

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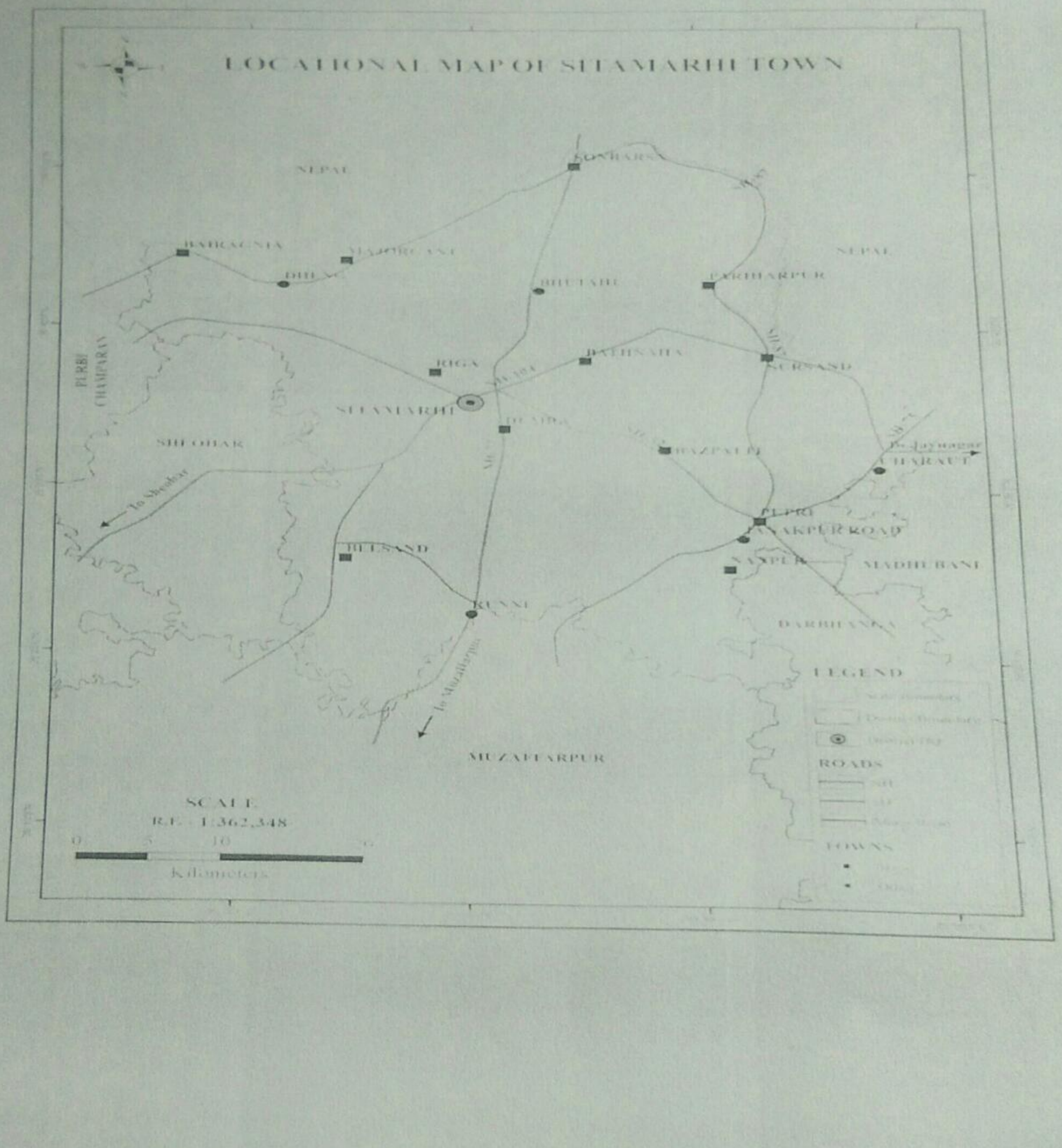
## STUDY AREA

The study area of present research work is Sitamarhi town which is the district headquarter of Sitamarhi district of Bihar.



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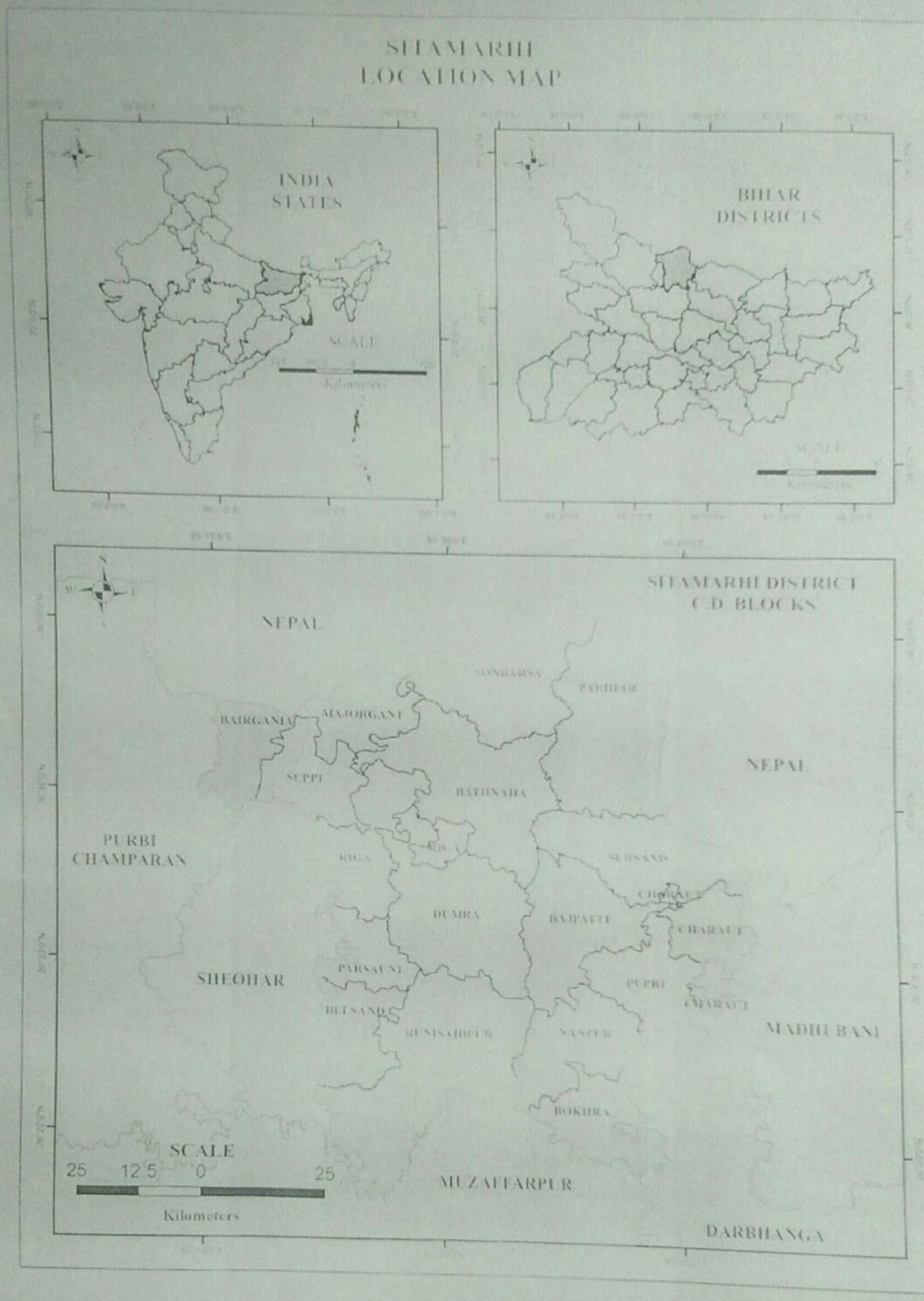

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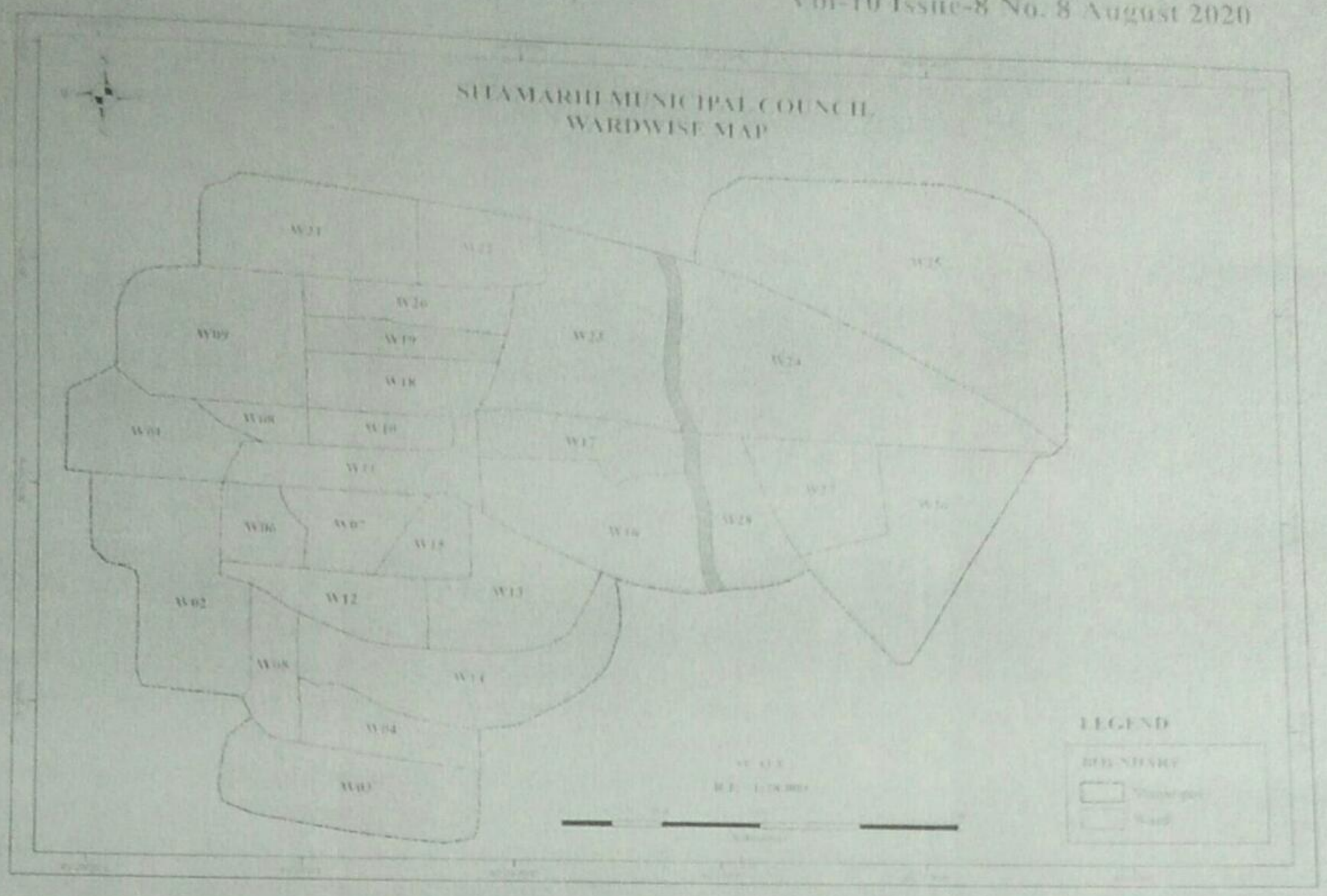


Sitamarhi district is situated in northern part of middle Ganga plain of Bihar. The town Sitamarhi is administrative unit (Municipal Council) of Dumra block and situated in the center of the block. National Highway 77 connects it to Muzaffarpur and Patna district to the South. State highways link it to Madhubani district in the east and Sheohar district in the west. The town Sitamarhi is situated on the Darbhanga-Narkatiaganj railway line and has the largest railway station of the district. There is another broad gauge track, running between Muzaffarpur and Sitamarhi. Sitamarhi municipality was constructed in 1882 with a municipal board consisting of 12 commissioners. At that time there were only 4 wards in the town. (**Bihar District Gazetteers Muzaffarpur, 1958**) Now the municipality is divided into 28 wards. Dumra Notified Town Area Committee was constituted in 1937. Sitamarhi urban agglomeration occupies Dumra Notified Town Area as a statutory town. At present most of the government offices of Sitamarhi district are situated in Dumra. Sitamarhi is located in Mithila cultural region which is a part of Tirhut Division of Bihar.

The study area, Sitamarhi municipal council is situated almost in the center of Sitamarhi district, within Dumra block and occupies an area of about 5 square kilometer. The shape of Sitamarhi municipal council (SMC) is almost rectangular. The SMC has maximum east-west extension of 4.5 km and maximum north-south extension of 3 km. The site of the town Sitamarhi is a flood free site on natural levee of river Lakhandei. The municipal council has rivarian situation on both side of the river Lakhandei and has an important location at the confluence of state highway and NH 77, and along Darbhanga-Narkatiaganj railway line.

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## OBJECTIVE

This study is aimed to find out the problems associated with provision and maintenance of urban amenities in small towns in general and in Sitamarhi town in particular. The study also tries to find out the reason behind different problems of urban amenities. Specific problems of urban amenities in small towns are also within the scope of this study.

## METHODOLOGY

This study is based on primary data and information collected from urbanites residing in Sitamarhi town through schedule and data and information collected through personal interview of ward members and municipal officers. Some information for this study has been collected through empirical observation by researcher. Secondary data for this study has been collected from different government and non-government journals, periodicals and census survey reports. These data have been analyzed with suitable methods to process information regarding problems of urban amenities.

## URBAN AMENITIES

Urban amenities are goods, services and facilities that people appreciate about their environment. These are services and facilities that make any town livable and comfortable. Urban amenities can be considered as public goods and services for collective consumption (Castells, 1977). Urban amenities means the facilities provided to urban population for a good, comfortable and healthy life (Kuntal Kishor, 2018). Michael Pacione (2009) has identified three basic characteristics of urban amenities; joint supply, non-excludability and non-rejectibility. Condition of urban amenities predicts the future growth of the town. Better amenities always attract population and investment. So, urban amenities are essential pre-requisite for socio-economic and physical growth of town. The provision of urban amenities in towns is one of the most important functions of welfare government. These are also essential for revenue generation. Equal and just distribution of urban facilities and services is a challenge for local governing bodies in towns of developing countries like India.

## PROBLEMS OF URBAN AMENITIES IN SMALL TOWNS (SITAMARHI)

Equal and just distribution of urban amenities and maintenance of its quality and quantity according to the need of urbanites is the main aim of government agencies and Urban Local Bodies (ULBs). The difference in demand and supply of urban amenities is due to several problems related with provision and maintenance of urban amenities. Small towns with small fund, low managerial and technical know-how of ULBs, unskilled workers face different problems than big towns where governing bodies and workers are skilled and trained and funds from public and private (or both) agencies received regularly. More or less, all small towns face similar problems of urban amenities. The problems of urban amenities in small towns (especially Sitamarhi town) have been categorized by Kuntal Kishor (2018) in two classes; Structural problems and Institutional problems.

| | | |
|---|---|---|
| (i) | **Structural Problems** | Inadequacy of services and facilities |
| | | Poor quality of services and facilities |
| | | Lack of civic sense in Urbanites |
| (ii) | **Institutional Problems** | Spatial and social variation in distribution of services. |
| | | Poor maintenance of services and facilities |
| | | Improper implementation of programme. |
| | | Overlap of the area of services with |




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| | | |
|---|---|---|
| | | parastatal agencies. |

Source: Unpublished PhD Thesis of Kuntal Kishor, Patna University, 2018.

### (i) STRUCTURAL PROBLEMS:

Structural problems are associated with the basic social and cultural structure of the town, characteristics of population and available infrastructure.

**Inadequacy of services and facilities**

The problem of inadequate services and facilities is due to lack of fund for development of necessary infrastructure. Most of the small towns in India face this problem and Sitamarhi town is not an exception. Problem of inadequate facilities and services in the town has been mentioned below.

1. Lack of number of workers in municipal council for sanitation work.
2. Inadequate fund for development of drainage and sewage.
3. Inadequate power for continuous supply of electricity.
4. Inadequate number of dustbins for storage of domestic waste.
5. Inadequate number of street lights.
6. Inadequate number of shopping mall and parking places.
7. Absence of sewage treatment plant.
8. Insufficient number of multi-speciality hospitals.
9. Insufficient infrastructure for industrial development.
10. Absence of footpath for pedestrian.
11. Absence of technical (Medical/Engineering) colleges in the town.
12. Inadequate infrastructure for water supply to slum dwellers.

Similar problems of inadequate urban amenities have been found in different small towns e.g. Bettiah (Md. Hussain Ansari, 1991) and Saharsa (Anant Bhagat, 2016).

**Poor quality of services**

The town Sitamarhi is one of the poor cities in Bihar in terms of quality of services provided here. The municipality and parastatal agencies of Bihar government (like PHED, Bihar Electricity Board, BSNL, DEO office and Banks etc) are responsible to provide physical, social and financial public amenities to the urban residents. These agencies are unable to provide the good quality services partially due to lack of fund and resources and partially due to lack of determination of the agencies to provide basic civic services to the residents and properly implement the plans and schemes regarding provision of basic urban amenities. Lack of managerial and technical knowhow in local bodies is also responsible for poor quality of services. Main problem of urban amenities in terms of its quality are following:

1. Lack of wide good quality roads.
2. Lack of facilities for pedestrian and street vendors (separate space on roads).
3. Lack of good quality institute for higher education.
4. Poor quality of drainage system in few pockets of slums of Sitamarhi.
5. Poor quality of community toilets.
6. Poor overall environmental condition and lack of beauty of urban landscape.




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7. Lack of good quality intensive and emergency care medical facility, for which town dwellers depend on SKMCH (Muzaffarpur) and PMCH (Patna) and others Hospitals outside the town.
8. Poor quality of sanitation services.
9. Poor quality of urban solid waste disposal (disposal without treatment along the Ring Road).
10. Poor quality of bus Depot (stand) and vehicles parking places.
11. Dustbins placed to collect Household solid wastes are too small to accommodate the domestic wastes of all household of the colony.

Poor quality of public utility services is a common problem in small towns of India. Aforesaid problems were also observed by O. P. Prasad in Buxar (2005) and Md. Hussain Ansari in Bettiah (1991).

**Lack of civic sense in Urbanites**

Alexander Badawy (1967) in his article "The civic sense of Pharaoh and urban development in ancient Egypt" put emphasis on importance of civic sense in urban residents in development and maintenance of any urban landscape. Lack of civic sense in residents of Sitamarhi town is expressed through their following behavior:

1. Many of the town dwellers throw solid waste in drain.
2. Urbanites in the town litter garbage on roads.
3. Sometime they do not follow traffic rules.
4. Town dwellers do not keep public property clean and sometime destroy it.
5. Many of the residents of town have illegal electricity connection to elude the electricity charges.

**(ii) INSTITUTIONAL PROBLEMS:**

Institutional problems of urban amenities are due to discrepancy in involved government institutions. More or less all small towns in India face similar institutional problems in provision and maintenance of urban amenities. Some of these problems found in Sitamarhi town have been discussed below.

**Spatial and social variation in distribution of services**

Intra-ward variations in distribution of services and facilities in study area are mainly due to the reason that the areas inhabited by influential person are better served than the other areas of ward. Inter-ward/Inter-colonial variation in distribution of facilities is mainly the result of ecological process of evolution of the town. During evolution of Sitamarhi town socially and economically backward class (laborer of unorganized sectors) settled in the area of low rental value. These areas became slum during gradual development of the town and these are the least served areas having lowest sanitation, drainage and toilet facility and temporary (kachcha) houses. So, inter-ward variation is result of social segregation processes. Almost all small towns in India face problem of unequal distribution of urban amenities like Sitamarhi town.

**Poor maintenance of services and facilities**

Urban amenities need to be regularly maintained for their long life and proper functioning. Maintenance of urban infrastructure, services and facilities is function of government agencies in Indian towns. In Sitamarhi town, like other

ISSN: 2278-4632
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small towns in India, regular maintenance of urban amenities is not performed due to following reasons:

1. Unwillingness of government agencies.
2. Lack of fund for renovation and maintenance of urban amenities.
3. Absence of public support for renovation activities.
4. Misuse of public properties by town dwellers.

**Improper implementation of programme**

Importance of small town is well recognized by the governments in India. There are many programmes launched by states and central government for development of small towns. Implementation of these programmes is task of executive bodies. But proper implementation of programmes related with development of urban amenities in small towns is not done due to:

1. Lack of technical and managerial knowhow in governing bodies.
2. Lack of determination for implementation of programmes.
3. Conflict between parastatal agencies.
4. Lack of fund for proper implementation of programmes.
5. Corruption and local politics.

Similar problems of improper implementation of programmes have been found by different scholars in different small towns of India.

**Overlap of the area of services with parastatal agencies**

"In all the cities, service delivery is fragmented, with multiple entities involved in each service. These entities are also often accountable to different departments of the state government, which means that reform also has to involve state governments. Fragmentation of responsibility of service delivery and its duplication are common phenomena."(**David Savage and Shubhagato Dasgupta**). Duplication of responsibilities creates confusion in government agencies and so provision of amenities to town dwellers is not done properly. Sometimes different agencies blame other agencies for irregular and poor quality of services and no agency take responsibility of the misdeeds. 'In Sitamarhi town supply of water is responsibility of both Municipality and Physical Health and Education Department (PHED). The duplication of functions of government bodies always lead to confusion in implementation of schemes. The clear division of function between different agencies of government is necessary for proper functioning of different bodies and better implementation of programmes and schemes' (Kuntal Kishor, 2018).

## CONCLUSION

Urban amenities are the facilities, services and infrastructure that people in town want to have for better life. Provision and maintenance of urban amenities in small towns of India has been a challenge for local governing bodies. The problems of urban amenities in small towns of India are different from the problems in big towns. Poor quality of services, inadequate services and facilities, lack of civic sense in urbanites together with malfunction of institutions involved in provision and maintenance of urban amenities are some of the problems universally found in small towns of India.




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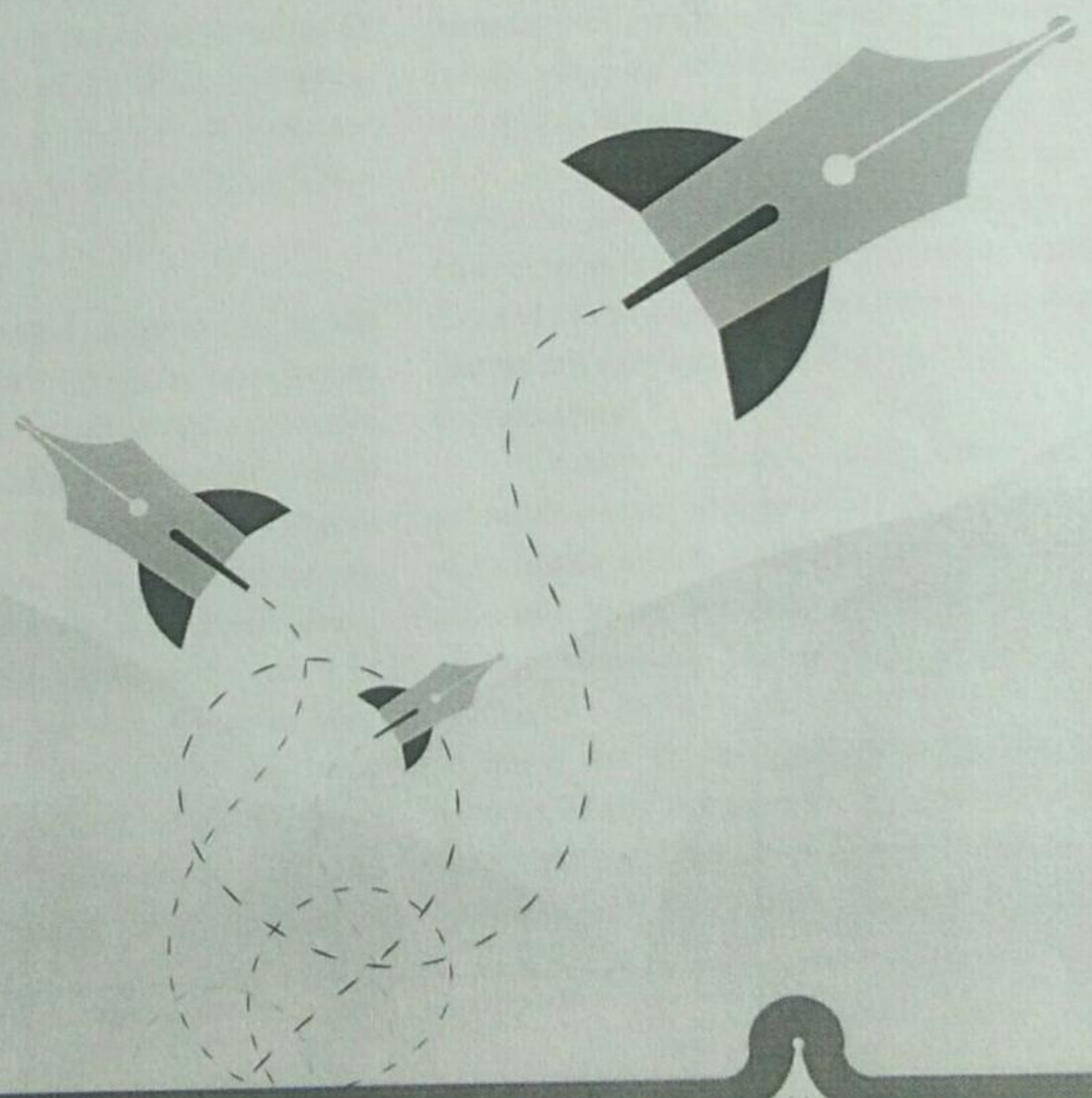
GOVT. OF INDIA- RNI NO. UPBIL/2014/56766
UGC Approved Care Listed Journal
ISSN 2348-2397
SIF

# शोध सरिता

An International Multidisciplinary Quarterly
Bilingual Peer Reviewed Refereed Research Journal

• Vol. 7 • Issue 27 • July to September 2020



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ISSN - 2348-2397
APPROVED UGC CARE

SHODH SARITA

SHODH SARITA
Vol. 7, Issue 27, July-September, 2020
Page Nos. 82-86

AN INTERNATIONAL BILINGUAL PEER REVIEWED REFEREED RESEARCH JOURNAL

# CREATIVE COMPONENTS MAKES CREATIVE ADVERTISING : AN ANALYSIS

Dr. Pradeep Kumar Srivastava*

## ABSTRACT

Creative components are means for helping creative people to final new and relevant ideas to carry their themes in advertising. Creative advertising has now become an indispensable activity in our economy and its significance is increasing year after year. Its need has arisen due to the sweeping changes in the life of everyone. Actually after economic liberalization Indian advertising industry witnessed a boom. The entry of many MNCs in India has further added new variety of feathers to the growth-cap of advertising. Advertising expenditure in India has been increasing rapidly. It is only because of creative advertising is considered one of the most vital areas of investment. The objective of the present study is to examine the different creative associations which make the advertisement creative.

**Keywords :** Creativity, Innovation, USP, Relevance, Execution, Incubation , Illumination

**Methodology**

The research work has been undertaken to explore requirements, impact and the analysis of creative association in advertising. This is descriptive in nature. In order to achieve the objectives of the study secondary sources of data have been used viz., Centre for Monitoring on Indian Economy (CMIE); FICCI- Price waterhouseCoopers report.

**Result**

There are different creative components which make advertising creative like creative association, creative idea, creative process etc. A number of creative associations that may be in the advertisement like Unique Selling Proposition, relevance, jingle, slogan, positioning, celebrity, execution, humor, branding etc. which makes advertisement creative. Preparation, incubation, illumination, and verification are four established stages of creative process. Creative idea, creative process and creative association are basic components of creative advertisement. Creative advertisement is now become necessary to exist and make competitive in the market with maximum profitability.

**Conclusion**

Creative advertising has now become an essential parameter to every type of advertisement in our economy. it will create the relevance of creative components that are capable to make an advertisement creative. The one of basic components are creative association like usp, relevance, jingle, slogan, branding, celebrity humor etc other components are creative ideas and creative process. Its need has emerged because of the major developments that are influencing the life of everybody.

**Introduction**

Economic reforms attempted as of late have achieved a great change in the economic environment. Advertising sector, alongside different segments of the economy, has additionally profited by and large by the change measures. The passage of MNCs, in India, combined with the battle of customary Indian corporate to make due in the market brought about expanded volume of ads from contending brands. Indeed, Indian advertising industry saw a genuine 'commercial boom' in post economic liberalization time. The section of MNCs

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in India has additionally added new plumes to the development top of advertising. Satellite TV stations have strengthened its development example and structure. The utilization of cutting edge devices and methods has incredibly improved its quality and execution. Promoting of budgetary administrations has injected new force and eagerness into advertising.

**Creative Components in Advertising**

Creative components are means for helping creative people to final new and relevant ideas to carry their themes in advertising. While creative advertising is referred to as an art which is original, relevant, noticeable, memorable and refreshing in its presentation. A creative packed advertisement should be pure, simple and honest in its presentation. The use of association is the most common creative problem solving techniques inexistence and the making of association is basic to the creative mind. Thus, associations are means for helping creative people to final new and relevant ideas to carry their themes.

The need for creative advertising is quiet from the fact that there are uncountable ads and commercials bombarding our daily lives, yet only a few of them are remembered as creative. The reasons for advertisements not being read as a self oriented approach rather than as market oriented approach and lack of creative approach. A creative advertisement, whether in terms of ideas or execution or both, will stand out, provoke interest, and bring prestige and attention. There is pure creativity, as in fine art, there is applied creativity. Thus advertising creativity is a sort of applied creativity. Creativity is simply a technique for producing ideas to achieve something new and relevant. Webstar[2] defines creativity as "the ability to bring something new in to existence". It is the most important aspect of the advertising effort because it determines success or failure for a marketer. Advertising with creative ideas requires a human touch and theme. Newness and relevance are the basic characteristics of creative ideas. To be more specific and relevant, each advertising agencies go with new creative ideas to ensure their prosperous marketing. Creativity in advertising is defined, by Hepner (1956)[1], as having two characteristics: first, the originality evident in the message communicated and in its presentation, and second, the improvement made in the life of consumers or effect on the consumer's standards of living.

The requirement for creative advertising hushes up from the way that there are uncountable promotions, advertisement and plugs assaulting our everyday lives, yet just a couple of them are recognized as imaginative. The explanations behind notices not being perused as a self situated methodology as opposed to as market arranged methodology and absence of innovative methodology. An innovative commercial, regardless of whether as far as thoughts or execution or both, will stick out, incite intrigue, and bring glory and consideration. There is unadulterated innovativeness, as in compelling artwork, there is applied imagination. In this way publicizing imagination is such an applied inventiveness. Imagination is essentially a procedure for creating thoughts to accomplish something new and important. Webstar2 characterizes creativity as "the capacity to bring something new in to presence". It is the most significant part of the promoting exertion since it decides achievement or disappointment for an advertiser. Promoting with inventive thoughts requires a human touch and subject. Originality and pertinence are the essential attributes of innovative thoughts. To be more explicit and applicable, each publicizing offices go with new inventive plans to guarantee their prosperous promoting. Inventiveness in publicizing is characterized, by Hepner (1956)1, as having two qualities: first, the creativity apparent in the message conveyed and in its introduction, and second, the improvement made in the life of purchasers or impact on the customer's ways of life.

There are different creative components which make advertising creative like creative association, creative idea, creative process etc. A number of creative associations that may be in the advertisement like Unique Selling Proposition, relevance, jingle, slogan, positioning, celebrity, execution, humor, branding etc. which makes advertisement creative.

**Objective of the Study**

The objectives of the present study are :

1. To explore the creative association in

advertisement

2. To highlight the determinants of creative advertising

**Literature Review**

Elms (1995)[3] has given two major components of creative strategy are first is message content and second is message execution.

Jewler and Drewniany (2001)[4] say that an ad "needs to contain a persuasive message that convinces people to take action". To be more creative, however, they suggest that an ad "must make a relevant connection with its audience and present a selling idea in an unexpected way.

William et. al. (2004)[5] says that effective ads work on two levels. First, they should satisfy consumer's objectives by engaging them and second, delivering a relevant message.

**Creative Ideas**

An idea must be novel and relevant to be creative. Both the qualities are as two wheels of two wheeler motor cycle. If one of them is not present in any idea, that will not be creative. Creative ideas are novel and relevant realities resulting from connection of old realities. Often this is by-product of analogical or metaphorical thinking.

Creative advertising ideas require some basic norms such as adaptability, durability, newness, oneness relevance, memorability and simplicity. This 'ADNORMS' are characteristic standard of quality found in the most c reative advertising ideas. Off-course, we could not ensure that all creative advertising ideas will satisfy or possess the entire above characteristic to meet standards of quality but they are considered as goal for the creative advertising mind. Marra (1990)[6] pointed out that creative advertising ideas were uniquically and strategically positioned in the target audience's mind. Their newness and rightness ensure their productivity which are durable and satisfier of market requirement. With above ADNORMS we can examine creativity in advertising ideas.

**Creative Process**

Joseph Wallas, who proposed that creative thinking proceeds through four phase: stage of creative process: preparation, incubation, illumination, and verification. Preparation is the phase during which the creative person does all the preliminary work. He thinks in a sort of free way, he collects he searches, listens to suggestions, and lets his mind wander. The stage of incubation is inferred from the fact that a certain period of time, ranging from a few minutes to months or years, elapses between the period of preparation and that of illumination[7]. This period may be variable length as the person turns to his everyday business. The third stage illumination presents the emergence of an idea or a solution to a problem. The creative individual after analyzing existing ideas and verifying the old one submit a solution to the best of his ability in respect of problem selected under creative process. The last stage of verification, at this stage actual working of the idea take shape and the creative individual find out the creative ideas as a final solution after verification. On the other hand Taylor retains Walla's four stages but also believes that creativity exists at five different levels..

Every models of the creative process are base on the steps in the creative process. The creative process is going through the stages of orientation, preparation, analysis, ideation, incubation, synthesis and verification. Thus, we can say that the primary objective of creative process is a person, a problem and a solution.

**Approach towards Advertising**

In India the main Advertising Convention was set up in Kolkata in 1960's. As per Dr. Keskar, The promoting ought to be Indian in thought and substance. In 1980, there was an extension in both electronic and print media. The idea of supported software engineers on TV was start presented for "Murmur Log" famous drama in 1983, at that point came "Buniyaad, Nukkad" and " Mahabharata" and "Ramayana" from 1986 ahead which was appeared in Doordarhan with no serious channels. 1990s was the year for satellite stations, which assisted the promoting scene with thriving completely fledged.

Subsequent to picking up Independence the matter of publicizing slowly began cutting a reasonable specialty in social and monetary arrangement of the nation. Notwithstanding, till 1970s Indian business sectors had restricted presentation to rivalry. Markets were practically vender arranged. In an economically

tight market, the dealer needs adverting with the sole reason for anticipating a picture of the venture in the brains of clients. The whole publicizing program is intended to suit the customer's likes instead of definitive clients. Consequently, promoting involves a little specialty in the whole range of showcasing procedure of the seller[8].

During this time, creative advertising becomes essential prerequisite to address the difficulty for advertising of a specific item. The customer is lord in free undertaking framework and his needs will decide handiness of items. In light of the current situation private associations as well as open endeavors will undoubtedly focus on the part of creative advertising to get the considerations of focused shoppers, and to get the most extreme consideration, they are offering items and administrations upheld by creative advertising. Thus, Creative advertising has become an imperative movement in our economy and its noteworthiness is expanding a seemingly endless amount of time after year. Its need has emerged because of the far reaching developments that are influencing the life of everybody. Creative advertising is presently an acknowledged force in the business world. Anyplace we go, we notice a plenty of notices around us, disclosing to us various messages. Inventive promoting gives the open the option to pick between numerous choices, numerous brands. It empowers shoppers to pick the best quality or the most minimal cost or the best blend of value and cost. The financial specialists everywhere on over the world have discovered that it is a powerful and productive investment.

**Findings**

Creative advertising has been characterized and examined by the different researchers with various method of examination in a given point of view. Various models have additionally been proposed to pass judgment on the imagination face to face, thought, ads and showcasing. Defenders of creative advertising have consistently concurred that creativity was essential prerequisite to sell or to set up each item in the serious market and it is result of creative components that will make the advertisement creative. Discussions and theories have been created to explain method of creativity and its significance. The accompanying segment presents the primary discoveries of the examination:

- Creative advertisement is now become necessary to exist and make competitive in the market with maximum profitability.
- Creative idea, creative process and creative association are basic components of creative advertisement.
- Creativity and innovation are two basic pillars of an advertisement for productivity and sustainability.
- Originality and imagination are useful in creativity and also expected to make feasible solution to real problems, despite profitability.
- Preparation, incubation, illumination, and verification are four established stages of creative process.
- Creative ideas are very dependent on these qualities of newness and relevance. Such creative ideas relating to advertisement possessed adaptability, durability, oneness, newness, relevance, memorability, and simplicity. Therefore, creative advertising ideas are uniquecally and strategically positioned in the target audience mind.

**Conclusion**

During the current period, imagination in promoting becomes essential prerequisite to address the difficulty for advertising of a specific item. The buyer is ruler in free endeavor framework and his needs will decide value of items.

Thus, creative advertising has now become an essential parameter to every type of advertisement in our economy. it will create the relevance of creative components that are capable to make an advertisement creative. The one of basic components are creative association like usp, relevance, jingle, slogan, branding, celebrity humor etc other components are creative ideas and creative process. Its need has emerged because of the major developments that are influencing the life of everybody. Planning, brooding, light and confirmation stages were important to produce inventive thoughts

along with this imaginative people must work in durable group to use their likely capacities.

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