

## Study of the Spectroscopic Analysis, Electronic Structures and Thermodynamic Properties of Ethyl benzene Using First-Principles Density Functional Theory<sup>1</sup>

Rabin Ghimire, Abhishek Rana Magar, Bishwo Basnet, Roshika Uprety, Kiran Pudasainee, & Krishna Bahadur Rai

### Abstract

This study describes the optimized molecular structure, spectroscopic analysis, electronic structure and thermodynamics properties of the ethylbenzene molecule using first-principles DFT/B3LYP method with 6-311++G(d,p) basis set. The C-H in-plane bending vibration is observed between 1400 and 1050  $\text{cm}^{-1}$ , while the C-H out-of-plane bending vibration is observed between 1000 and 675  $\text{cm}^{-1}$ . The benzene ring has the most negative potential that corresponds to the attraction of proton due to concentrated electron density while the moderate positive potential is localized closed to the hydrogen atom. Analysis of the HOMO and LUMO in ethylbenzene anticipates an energy disparity of 6.3028 eV, a value closely matching the energy gap derived from DOS calculations. Mulliken charge analysis of the ethylbenzene molecules gives the information that all the hydrogen atom corresponds to the positive charges while all the carbon atom except C3 corresponds to the negative charge and the values of the global parameters such as hardness, chemical potential, electronegativity, electrophilicity index, softness are found to be 3.1514 eV, -3.5979 eV, 3.5979 eV, 2.0538 eV and 0.3173  $\text{eV}^{-1}$  respectively. Various thermodynamic parameters such as heat capacity at constant volume, heat capacity at constant pressure, total internal energy, enthalpy and entropy, exhibit a rising

<sup>1</sup> Cite this article as: Ghimire, R., et al. (2024). *Contemporary Research: An Interdisciplinary Academic Journal*, vol. 7 (1); DOI: <https://doi.org/10.3126/craiaj.v7i1.67259>

Rabin Ghimire, Abhishek Rana Magar, Bishwo Basnet, & Roshika Uprety, Department of Physics, Patan Multiple Campus, Tribhuvan University; Kiran Pudasainee & Krishna Bahadur Rai, Department of Physics, St. Xavier's College, Kathmandu, Nepal.

Email: [krishnarai135@gmail.com](mailto:krishnarai135@gmail.com), [krishna.rai@pmc.tu.edu.np](mailto:krishna.rai@pmc.tu.edu.np) (corresponding author)

Article history: Received on February 21, 2024; Accepted on may 18, 2024; Published on June 25, 2024  
Peer reviewed under the authority of CRAIAJ, academic journal of Ghodaghodi Multiple Campus, Kailali, Nepal, with ISSN 2717-4611 (Print) and ISSN 2717-462X (Online).

© 2024 CRAIAJ, A Star Rated Journal Indexed in Nepjol



Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

trend with increasing temperature whereas Gibbs free energy shows an inverse relationship with temperature variation.

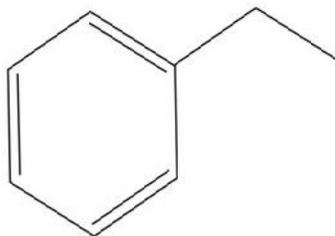
**Keywords:** Density functional theory, Electronic structure, Ethylbenzene, Thermodynamics parameters, Vibrational analysis

### Introduction

Ethylbenzene ( $C_8H_{10}$ ) is a hydrocarbon compound with the molecular formula  $C_8H_{10}$ , characterized by the substitution of a benzene ring with an ethyl group. The molecule consists of a six-carbon benzene ring, where each carbon atom forms a sigma bond with two neighboring carbon atoms and one hydrogen atom. One of the carbon atoms in the benzene ring (Rai et al., 2024) is further bonded to an ethyl group ( $C_2H_5$ ), replacing one of the hydrogen atoms. The ethyl group consists of two carbon atoms and five hydrogen atoms, and it extends outward from the benzene ring. Overall, ethylbenzene has a planar, aromatic structure due to the resonance of its benzene ring, contributing to its stability (Wang et al., 2012). This compound is commonly used as an industrial solvent (Francis et al., 1946) and is an essential precursor in the production of styrene, a monomer used in the synthesis of various plastics and synthetic rubbers. It is a colorless, extremely flammable liquid with a gasoline-like odor (Zhou et al., 2022). In the petrochemical industry, this monocyclic aromatic hydrocarbon is crucial as a reaction intermediate in the synthesis of styrene, which is the starting point for polystyrene, a widely used plastic (Rijal et al., 2022). The First Principles calculations are widely employed for investigating electronic structure and ascertaining diverse properties (Gauli et al., 2023).

#### Figure1

*Chemical structure of ethylbenzene*



With the use of Density Functional Theory (DFT) techniques, several research papers and articles about  $C_8H_{10}$  have been published in recent years. Fan et al., (2015) used DFT in the dehydrogenation of ethylbenzene to styrene with carbon dioxide ( $CO_2$ ) over vanadium oxide ( $V_2O_5$ ). The result of the study showed that among all three lattice oxygen sites on  $V_2O_5$ , O(1) site is the most active site for the dehydrogenation of ethylbenzene. Lattice oxygen O(1) is removed from the lattice after styrene is produced by the emission of water ( $H_2O$ ). Since  $CO_2$  is a soft oxidant having a relatively high activation energy it can't re-oxidized the defective  $V_2O_5$  in time which causes the catalyst to gradually deactivate. Noei et al., (2017) studied the absorption of ethylbenzene molecules on the surface of Boron Nitride Nanotubes (BNNTs) and the subsequent doping of Si, P, S, and O atoms in the nanotube structure using DFT. The study concluded that it is possible to modify the nanotubes as a semiconductor but the result shows that BNNT is not a suitable absorbent for ethylbenzene. Similarly, using DFT with 631+G(d, p) basic set by Zhou et al., (2022) for the study of ethylbenzene in the presence of an external electric field predicts that the energy of  $C_8H_{10}$  increases on increasing electric field along a certain direction whereas the barrier of potential energy for dissociation decreases. However, the equilibrium configuration, vibrational analysis, electronic properties and thermodynamic properties of ethylbenzene using first-principles analysis with the basic set 6-311++G(d, p) have never been investigated before and it is now crucial and significant for additional research. Thus, the purpose of this study is to obtain a comprehensive knowledge of the optimized molecular behavior, vibrational analysis, electronic structures and thermodynamic analysis of ethylbenzene using DFT with B3LYP/6-311++G(d, p) basis set together with GaussSum 3.0 and Moltran software package.

### Computational details

All the quantum chemical calculations of the  $C_8H_{10}$  molecule were performed using the Gaussian09W program. GaussView 6.0 was utilized for both the analysis and molecular viewing of the results. The selected molecule's geometry was initially optimized using DFT/B3LYP method with the basis set 6-311++G(d, p) on the potential energy surface with complete relaxation. The optimized structural parameters were then used to compute the vibrational behavior (wavenumbers). For calculating the molecule electrostatic potential and electronic structure such as highest occupied molecular orbitals and lowest

unoccupied molecular orbital(HOMO-LUMO) energies and density of State(DOS) spectrum, the DFT method using the same basis set has been proposed. The GaussSum 3.0 program was used to observe the DOS spectrum. Similarly, the required data of the thermodynamics properties are obtained from the Moltran software and the graph are designed at the OriginPro9.0 software.

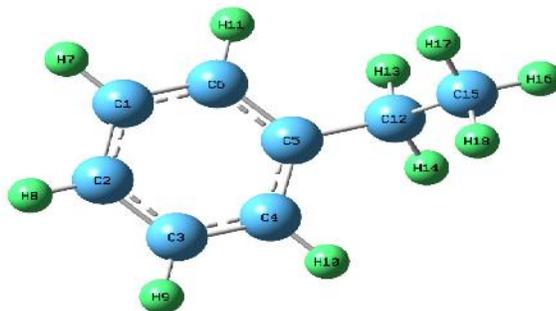
## Result and Discussion

### Optimized molecular geometry

The Gaussian 09W program uses geometrical optimization to get the minimum energy configuration of the ethylbenzene molecules. Figure 2 illustrates the optimized molecular structure of ethylbenzene molecule in a neutral state, with atomic numbering. The stability of optimized geometry is confirmed by the fact that all of the computed wave numbers are positive.

#### Figure 2

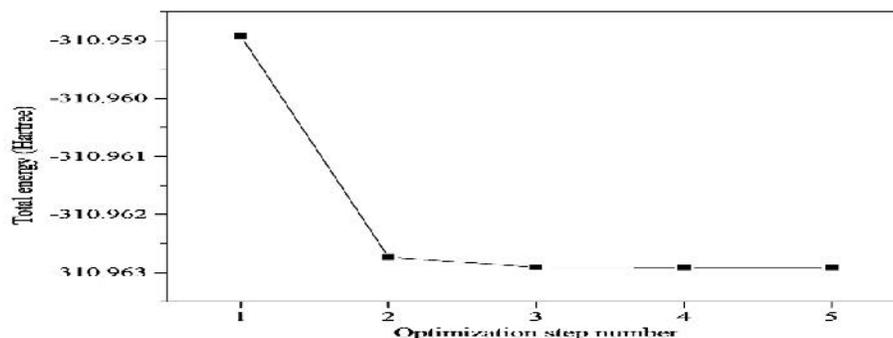
*Optimized structure of ethylbenzene with numbering of atoms*



The result of the total energy optimization process steps for the ethylbenzene molecules using DFT calculations is indicated by the figure 3 showing the relationship between total energy and optimization step numbers. From the figure 3, it is clear that the entire energy optimization phenomenon takes place in five different stages to set stable energy conformations and it starts from the energy of -310.9589 Hartree and gets optimized in the energy -310.9629 Hartree.

#### Figure 3

*Plot for optimization steps number vs total energy*

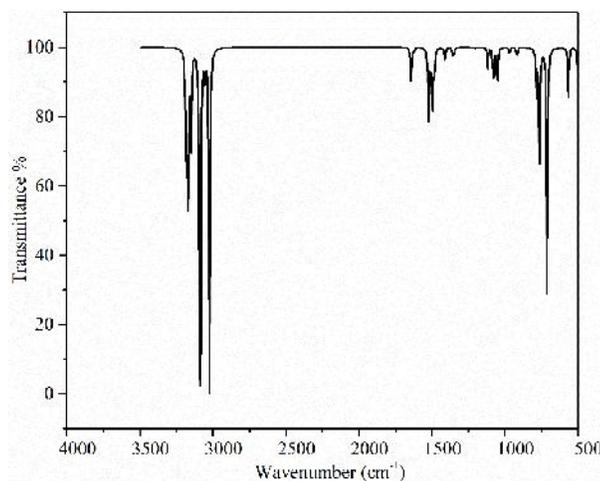


### Vibrational analysis of ethylbenzene molecules in neutral form

The ethylbenzene molecule is composed of 18 atoms having total number of fundamental modes of vibrations 48 ( $\nu_{\text{vib}}$ )( $3N-6$  for non-linear) in which it contains 33 in-plane vibrations, ( $A' = 2N-3$ ) and 15 out-of-plane vibrations, ( $A'' = N-3$ ). Figure 4 shows the FT-IR transmittance spectrum of different vibration modes of ethylbenzene in the range  $500-3500 \text{ cm}^{-1}$  and it indicates the relationship between the frequency and wavelength of infrared light (transmittance or absorption) which is a result of matter interaction with infrared radiation (Sharma et al. 2018; Wang et. al., 2012).

**Figure 4**

*IR spectroscopy for neutral ethylbenzene molecule*



Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

### **C-H Stretching vibration**

As we know each chemical bond oscillates at a certain frequency that is associated with a particular energy level. Any chemical bond's oscillation frequency is proportional to its wave number, which is expressed in units per centimeter (Limbu et al., 2024). Generally, in hetero aromatic compounds the C-H stretching vibration is expected to occur in the region 3100-3000  $\text{cm}^{-1}$  (Ludwig et al. 2018). In our work, figure 4 from FT-IR spectrum shows that the C-H stretching of the ethylbenzene molecule which are found to be occurred in the region of 3024  $\text{cm}^{-1}$ , 3087  $\text{cm}^{-1}$  and 3171  $\text{cm}^{-1}$ . The C-H in-plane and out-of-plane bending vibrations generally lie in between the region 1300-1000  $\text{cm}^{-1}$  and 900-650  $\text{cm}^{-1}$  respectively (Sharma et al., 2018; Amalanathan et al., 2023). From the same figure 4, C-H in-plane bending vibrations occur in the regions 1050  $\text{cm}^{-1}$ , 1078  $\text{cm}^{-1}$ , 1120  $\text{cm}^{-1}$  and 1358  $\text{cm}^{-1}$ . Additionally, C-H out-of-plane bending vibrations are found to be occurred in the region 714  $\text{cm}^{-1}$ , 763  $\text{cm}^{-1}$  and 917  $\text{cm}^{-1}$  in the same FT-IR spectrum.

### **C=C vibration**

C=C vibration usually occurs in the spectral region of 1400-1625  $\text{cm}^{-1}$  (Ludwig et al., 2018). Figure 4 in our study shows that C=C vibration occurs in the region 1407  $\text{cm}^{-1}$ , 1498  $\text{cm}^{-1}$ , 1526  $\text{cm}^{-1}$  and 1645  $\text{cm}^{-1}$ .

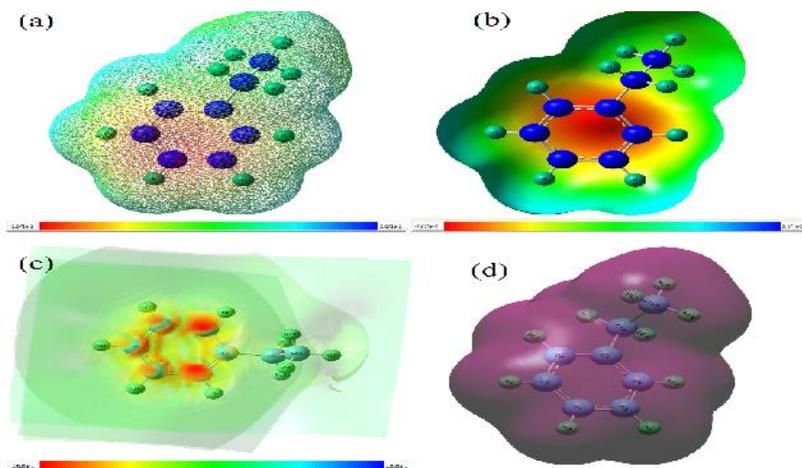
### **Molecular electrostatic potential(MEP), electrostatic potential(ESP) and electron density(ED)**

For predicting the charge distribution of the molecule, the Molecular Electrostatic Potential (MEP) map is used in which it identifies the compound's reactive site in the event of an electrophilic or nucleophilic assault (Kenouche et al., 2022). Figures 5(a) and 5(b) show the MEP map, Figure 5(c) shows the electrostatic potential (ESP) map and figure 5(d) shows the electron density (ED) map of the title molecule in neutral state. It describes the net electrostatic impact of the molecule's total charge distribution (electron + proton) and is related to electronegativity, dipole moments, chemical reactivity and partial charges. It provides a visual method for understanding the relative polarity of the molecule (Sangeetha et al., 2017).

#### **Figure 5**

(a) Mesh view (b) solid view of molecular electrostatic potential (c) electrostatic potential and (d) electron density mapping of ethylbenzene

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>



The potential values of the molecules range in the order: red < orange < yellow < green < blue (Ojha et al., 2023). The potential of our compound ethylbenzene ranges from  $-2.671 \times 10^{-2}$  (red) to  $2.671 \times 10^{-2}$  (blue) as shown in the figure 5(a) and 5(b). We can analyze that the benzene ring has the most negative potential that leads to the attraction of proton due to the concentrated electron density while the moderate positive potential is localized closed to the hydrogen atom and corresponds to the proton's repulsion by low electron density, which is reflected by the blue region. For ESP as shown in figure 5(c) the potential ranges from  $-2.635 \times 10^{-2}$  (red) to  $2.635 \times 10^{-3}$  (blue) which reflects that the negative potential is hanging out around the benzene ring because it is more prone to electrophilic attacks, showing up as a yellowish region. Meanwhile, the rest of the surface is rocking a localized positive potential, signaling its inclination for nucleophilic attacks. Similarly, figure 5(d) represent the electron density of the title molecules which gives us an idea for indicating the probability of an electron to be present at a specific location as well as about the uniform charge distribution.

#### HOMO and LUMO analysis

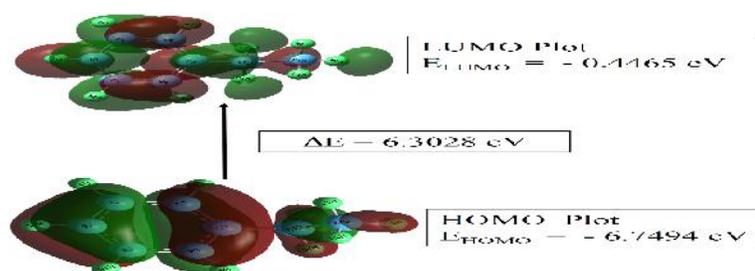
The HOMO is the highest energy molecular orbital that consists of electrons and act as an electron donor while the LUMO is the next lowest energy orbital that is empty and accept electrons as an electron acceptor. It is the lowest energy place to excite an electron. The production of a transition state is caused by an interaction between the

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

reactants' frontier orbitals (HOMO and LUMO), according to the frontier molecular orbital theory (Joshi et al., 2013). The energy difference between HOMO and LUMO orbital is called energy gap that is an important stability index for structure. Because it is a measure of electron conductivity and it is a key parameter in defining molecular electrical transport features. The lower the gap value, the higher the electronic transition, and vice versa (Francis et al., 1946; Limbu et al., 2024). Figure 6 shows the HOMO - LUMO plot with the frontier orbital energy gap for the ethylbenzene molecule. The obtained information regarding the energy of HOMO and LUMO are -6.7494 eV and -0.4465 eV respectively, such that the energy difference = 6.3028 eV.

**Figure 6**

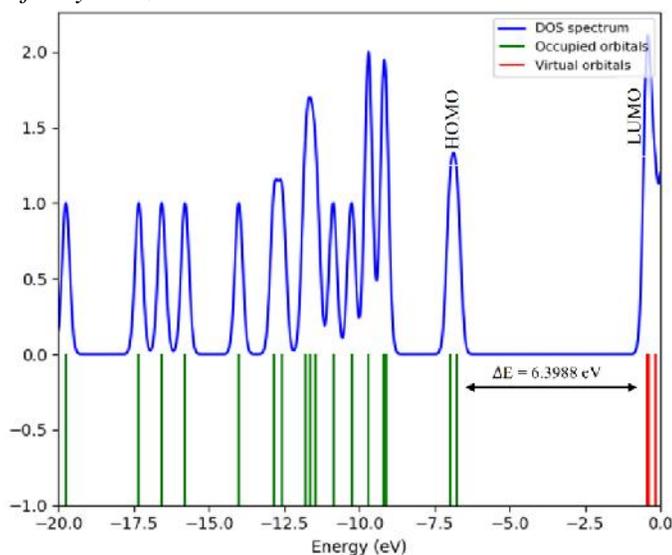
*Plot of HOMO-LUMO energy difference*



### Density of states (DOS)

Density of states spectrum is used to stimulate electrons from the valence band to the conduction band (Khalili et al., 2021; Khadka et al., 2023). Using the GaussSum 3.0.2 package with the full width at half maximum (FWHM) of 0.3 eV, the DOS spectrum for the titled molecule was obtained. It emphasizes how essential electrons are to the valence and conduction bands (O'Boyle et al., 2008; Shin et al., 2016). The DOS spectrum in figure 7 provides a clear explanation about the availability of multiple states at various energy levels. A positive number on the DOS represents a bonding contact, a negative value represents an anti-bonding interaction, and a zero value represents no bonding interaction (Abraham et al., 2018). A high-intensity DOS at different energy levels indicates the presence of numerous occupation states (Rijal et al., 2022). The energy gap, according to Koopmans' theorem, is the difference between LUMO and HOMO energy. Therefore, the energy gap seen in the DOS spectrum i.e. 6.3988 eV and the HOMO-LUMO gap i.e. 6.3028 eV are comparable and well-coordinated.

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

**Figure 7***Density of States of ethylbenzene***Global reactivity parameters**

By the use of ionization potential and electron affinity values we can obtain the global parameters such as hardness ( $\eta$ ), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), global electrophilicity or electrophilicity index ( $\omega$ ), softness ( $S$ ). The global hardness, is a measure of a chemical system's resistance to polarization or electron cloud deformation caused by minor disruptions during a reaction. It is closely linked to the system's stability and reactivity. The softness is the reciprocal of the hardness. The chemical potential ( $\mu$ ) of a molecule indicates its capacity for participating in chemical reactions or undergoing chemical changes. The potential energy emitted or absorbed during a chemical reaction may be determined using quantum chemical characteristics like electronegativity ( $\chi$ ). A molecule's capacity to take in electrons can be determined by looking at its electrophilicity index ( $\omega$ ). In chemical processes, it helps in predicting a molecule's reactivity towards nucleophiles. (El-Saady et al. 2023, Rai, et al., 2021).

Using Koopmans's Theorem (Chand et al., 2015), we can define  $I$ ,  $A$ ,  $\eta$ ,  $\mu$ ,  $\chi$ , and  $S$  as, Where ionization potential,  $I = -E_{\text{HOMO}}$  and electron affinity,  $A = -E_{\text{LUMO}}$

$$\text{Hardness of the molecules } (\eta) = \frac{1}{2}(I - A)$$

$$\text{Chemical potential } (\mu) = -\frac{1}{2}(I + A)$$

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

$$\text{Electronegativity}(\chi) = \frac{1}{2}(I + A)$$

$$\text{Electrophilicity index} (\omega) = \frac{\mu^2}{2\eta}$$

$$\text{Softness} (S) = \frac{1}{\eta}$$

Using the above equations, Table 1 shows the calculated values of ethylbenzene molecule's hardness ( $\eta$ ), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), global electrophilicity or electrophilicity index ( $\omega$ ), softness (S) and they are found to be 3.1514 eV, -3.5979 eV, 3.5979 eV, 2.0538 eV and  $0.3173\text{eV}^{-1}$  respectively. Large HOMO-LUMO gap indicates hard molecules while small HOMO-LUMO gap indicates soft molecules when taking chemical hardness into account. The hardness of a molecule is a good thing and is related with stability (Chattaraj et al., 2003). With a huge HOMO-LUMO gap and a very small softness value from the Table 1 makes it clear that the molecule under consideration is chemically hard. In general, a molecule with a higher negative chemical potential is more likely to react or take part in chemical processes. Therefore, in our study, ethylbenzene's chemical potential's negative value could indicate a particular reactivity or tendency to undertake reactions given at the right circumstances. Strong electrophiles have a value greater than 1.5 eV, moderate electrophiles have a value between 0.8 eV and 1.5 eV, and marginal electrophiles have a value less than 0.8 eV (El-Saady et al. 2023). The ethylbenzene molecule exhibits electrophiles value of 2.0538 eV which lies on the strong electrophiles range. So, the result of electrophilicity index as mentioned in the table 1 for ethylbenzene molecule suggests a strong electrophilic character. A higher value of electrophilicity index indicates the higher electrophilic behavior informing that it will receive electrons in a reaction more frequently.

**Table 1**

*Global reactivity parameters and energy values of ethylbenzene molecule*

Property	Energy value
$E_{\text{HOMO}}$ (eV)	-6.7494
$E_{\text{LUMO}}$ (eV)	-0.4465
$E_{\text{HOMO}} - E_{\text{LUMO}}$ gap (eV)	6.3028
chemical hardness ( $\eta$ ) (eV)	3.1514

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

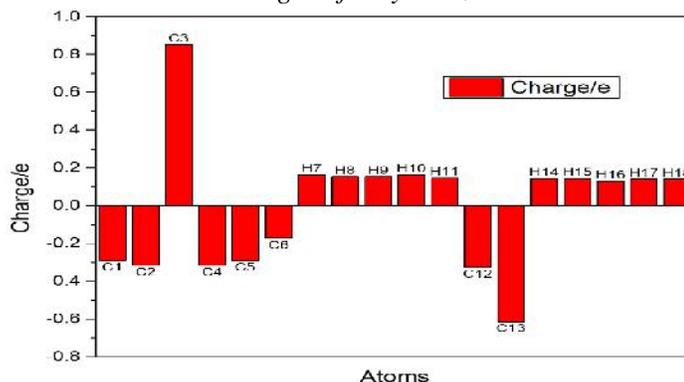
chemical potential ( $\mu$ ) (eV)	-3.5979
electronegativity ( $\chi$ ) (eV)	3.5979
electrophilicity index ( $\omega$ ) (eV)	2.0538
softness (S) ( $\text{eV}^{-1}$ )	0.3173

### Mulliken atomic charges

The electrical charge of the atom resolved the bonding structure and molecule shape. Figure 8 shows the Mulliken atomic charge values which play a vital role in quantum chemical calculation because they affect dipole moment, electronic structure, molecular polarizability, and many other aspects of molecular systems ([Amalanathan et al., 2023](#)). In ethylbenzene molecules all the hydrogen atom possesses positive charge and all the carbon atom except C3 possess negative charges.

### Figure 8

*Histogram of calculated Mulliken charges of ethylbenzene molecule*



In Mulliken charges, positive values indicate a net loss of electrons while negative values indicate a net gain of electrons. From the above figure 8, we can conclude that H10, C3 and H7 are more acidic due to more positive charges ([Amalanathan et al., 2023](#)).

### Thermodynamic analysis

The thermodynamic analysis of ethylbenzene molecule was performed using B3LYP/6-311++G(d, p) basis sets following the Moltran software program. For varying temperatures, the thermodynamic parameters including heat capacity at constant volume ( $C_V$ ), heat capacity at constant pressure ( $C_p$ ), total internal energy (U), enthalpy (H), entropy (S) and Gibbs free energy (G) were determined.

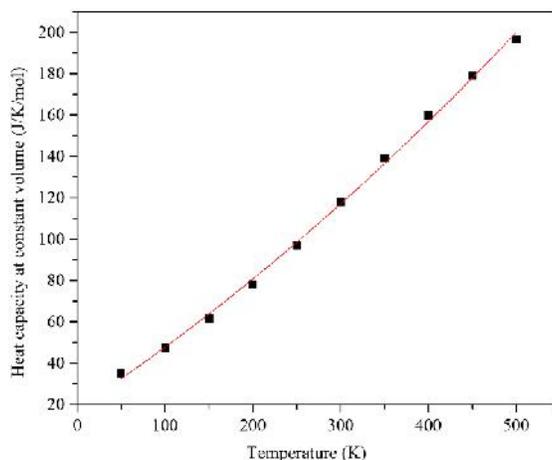
Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

Figure 9 shows the graph of correlation of heat capacity at constant volume ( $C_v$ ) with the temperature. Increasing rate is gradual till the temperature 200K but after that there is a slight deflection in the increasing rate of heat capacity with increase in temperature. The correlation equation between heat capacity at constant volume and temperature has been fitted by quadratic (polynomial) formula and the corresponding fitting factor ( $R^2$ ) for this is equal to 0.9977. The corresponding fitting equation is

$$C_v = 18.2308 + 0.2786T + 1.6940 \times 10^{-4} T^2$$

**Figure 9**

*Correlation plot of heat capacity at constant volume ( $C_v$ ) with different temperatures*



The correlation graph of temperature dependence of heat capacity at constant pressure ( $C_p$ ) of the molecule is shown in the figure 10 below which illustrates the nature that the value of  $C_p$  goes on gradual increment at a slow rate with increase in the temperature. **This quantity is positively correlated with temperature.** The fitting factor ( $R^2$ ) is found to be 0.9977 for heat capacity at constant pressure ( $C_p$ ) and its corresponding fitting equation is

$$C_p = 26.5496 + 0.2786T + 1.6945 \times 10^{-4} T^2$$

**Figure 10**

*Correlation plot of heat capacity at constant pressure ( $C_p$ ) with different temperatures*

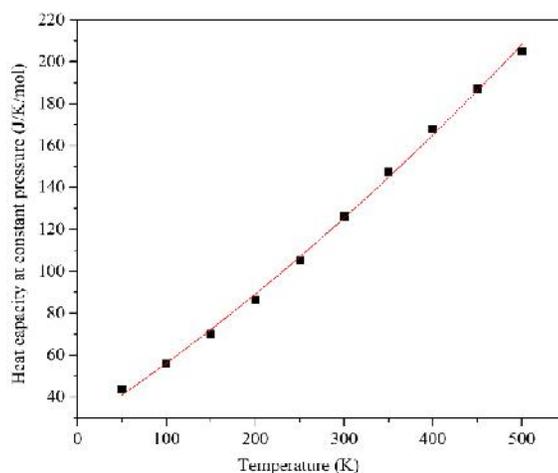
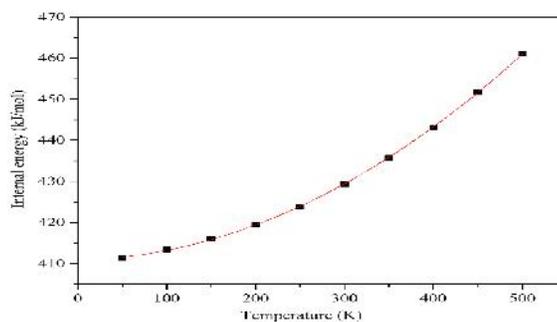


Figure 11 gives the graph of correlation of internal energy ( $U$ ) with the temperature of ethylbenzene molecule and it indicates that the total internal energy ( $U$ ) of the titled molecule increases with increase in temperature. The values of energy increase gradually within the temperature range 50K-200K but after that range, the nature of the curve show the fast-increasing rate of the values of the internal energy with increase in temperature. The correlation equation gives the corresponding fitting factor ( $R^2$ ) equal to 0.9998. **This quantity is also positively correlated with temperature.** The fitting equation for this correlation is

$$U = 410.8637 + 0.0045T + 1.9136 \times 10^{-4} T^2$$

**Figure 11**

*Correlation plot of internal energy ( $U$ ) with different temperatures*



Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

From figure 12, we see that the correlation of enthalpy (H) with temperature of the molecule and it is gradually increasing as the temperature increases. This reveals that the title molecule has greater flexibility in changing their own thermodynamic system in response to temperature (Chand et al., 2015). The values of R<sup>2</sup> is found to be 0.9999 and its fitting equation for this correlation is

$$H = 410.8638 + 0.0128T + 1.9136 \times 10^{-4} T^2$$

**Figure 12**

*Correlation plot of enthalpy (H) with different temperatures*

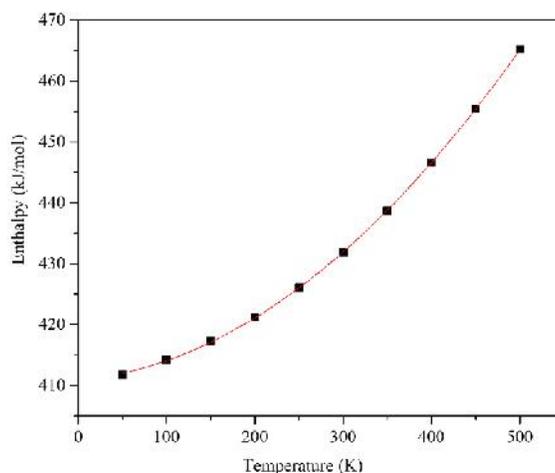
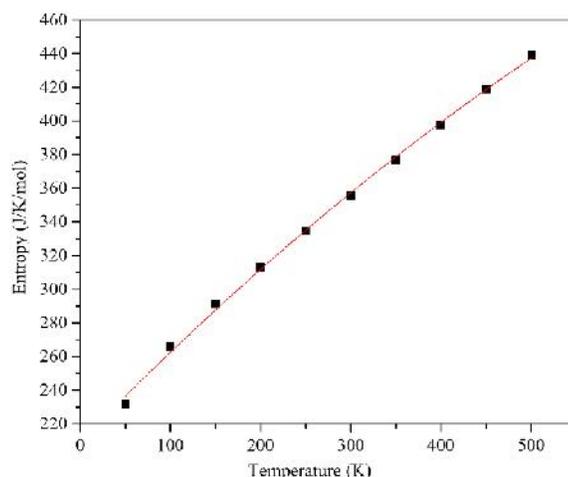


Figure 13 shows the correlation graph of temperature dependence of entropy (S) of the molecule and it illustrates that as the temperature rises, the entropy (S) of the molecule increases. When the temperature increases from the lower value to a higher one, there is a sudden increase in the entropy between the temperature 50K-100 K but after that range of temperature there is a decrease of the increase in the value of entropy. The correlation fitting factor (R<sup>2</sup>), as determined by the correlation equation, is 0.9981. There is also a positive correlation between this entropy and temperature. This correlation's fitting equation is

$$S = 209.5428 + 0.5485T - 1.8639 \times 10^{-4} T^2$$

**Figure 13**

*Correlation plot of entropy (S) with different temperatures*

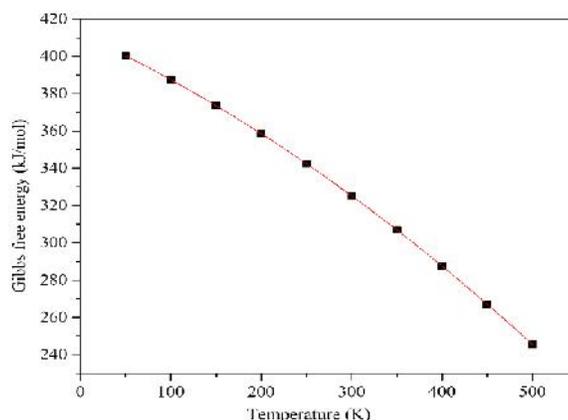


The Gibbs free energy correlation with temperature is fitted using quadratic formula and it is shown in Figure 14. It clearly shows that the Gibbs free energy ( $G$ ) of ethylbenzene molecule decreases steeply as increase in temperature and it is due to the reason that when the entropy term is greater than the enthalpy terms the overall value of Gibbs free energy becomes negative leading to a spontaneous process. With increase in temperature the entropy term becomes more dominant, leading to a decrease in Gibbs free energy ( $G$ ). The fitting factor ( $R^2$ ) is found to be 0.9999 and the corresponding fitting equation is

$$G = 412.0906 - 0.2244T - 2.1748 \times 10^{-4} T^2$$

**Figure 14**

*Correlation plot of Gibbs free energy ( $G$ ) with different temperatures*



The thermodynamic functions mentioned above are increasing with increase in temperature except Gibbs free energy which is due to the fact that the temperature causes an increase in the molecular vibrational intensities (Amalanthan et al. 2023; Limbu et al., 2024). In our present work, when the temperature increases from 50K – 500K, the thermodynamic function like heat capacity at constant volume ( $C_V$ ), heat capacity at constant pressure ( $C_p$ ), total energy (U), enthalpy (H), entropy (S) increase. The variations in enthalpy and entropy showed that the molecule could alter its own thermodynamic system more easily in response to temperature (Chand et al., 2015).

### Conclusion

In this study, we examined the vibrational properties, electronic structure and thermodynamics properties of the ethylbenzene molecule. The molecule needs five optimization steps to be completely optimized. Vibrational analysis of ethylbenzene with a neutral charge indicated that spectra between  $1400$  and  $1050\text{ cm}^{-1}$  correspond to C-H in-plane bending vibrations, whereas spectra between  $1000$  and  $675\text{ cm}^{-1}$  correspond to C-H out-of-plane bending vibrations. The study also found that the correlations between electron density, molecule charges orientation and structural activity by mapping MEP, ESP and ED. These analyses provided useful information about the distribution of electron density within the molecule, revealing that the negative potential is concentrated around the benzene ring, indicating a more electrophilic region, while the positive potential is found on the hydrogen atom, indicating a nucleophilic region. HOMO and LUMO analysis of ethylbenzene predicts the energy difference of  $6.3028\text{ eV}$  which is nearly equal with the energy difference obtained from DOS calculations. Mulliken charge

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

analysis of the ethylbenzene molecules gives the information that all the hydrogen atom corresponds to the positive charges while all the carbon atom except C3 corresponds to the negative charge. The values of the global parameters such as hardness ( $\eta$ ), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), global electrophilicity or electrophilicity index ( $\omega$ ), softness ( $S$ ) are found to be 3.1514 eV, -3.5979 eV, 3.5979 eV, 2.0538 eV and 0.3173 eV<sup>-1</sup> respectively. Furthermore, the thermodynamics analysis of the ethylbenzene molecule demonstrates that all the thermodynamic functions such as heat capacity at constant volume ( $C_V$ ), heat capacity at constant pressure ( $C_p$ ), total energy ( $U$ ), enthalpy ( $H$ ), entropy ( $S$ ) increase with increase in temperature whereas Gibbs free energy show the opposite behavior.

### References

- Abraham, C. S., Prasana, J. C., Muthu, S., & Raja, M. (2018). Quantum computational studies, spectroscopic (FT-IR, FT-Raman and UV-Vis) profiling, natural hybrid orbital and molecular docking analysis on 2, 4 Dibromoaniline. *Journal of Molecular Structure*, 1160, 393-405. <https://doi.org/10.1016/j.molstruc.2018.02.022>
- Amalanathan, M., Brintha, T., Sijana, S., Babu, P. J., & Mary, M. S. M. (2023). Identification of interaction of 1, 2, 3, 6-Tetrahydro-2, 6-dioxo-4-pyrimidinecarboxylic acid using DFT studies, molecular docking, biological activity and topology analysis for biological applications. *Chemical Physics Impact*, 7, 100393. <https://doi.org/10.1016/j.chphi.2023.100393>
- Chand, S., Al-Omary, F. A., El-Emam, A. A., Shukla, V. K., Prasad, O., & Sinha, L. (2015). Study on molecular structure, spectroscopic behavior, NBO, and NLO analysis of 3-methylbezothiazole-2-thione. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 146, 129-141. <https://doi.org/10.1016/j.saa.2015.03.068>
- Chattaraj, P. K., Nath, S., & Maiti, B. (2003). Reactivity descriptors. *Computational medicinal chemistry for drug discovery*, 295-322.
- El-Saady, A. A., Roushdy, N., Farag, A. A. M., El-Nahass, M. M., & Abdel Basset, D. M. (2023). Exploring the molecular spectroscopic and electronic characterization of nanocrystalline Metal-free phthalocyanine: a DFT investigation. *Optical and Quantum Electronics*, 55(7), 662. <https://doi.org/10.1007/s11082-023-04877-8>
- Fan, H., Feng, J., Li, X., Guo, Y., Li, W., & Xie, K. (2015). Ethylbenzene dehydrogenation to styrene with CO<sub>2</sub> over V<sub>2</sub>O<sub>5</sub> (001): a periodic density

Full text can be downloaded: <https://www.nepjol.info/index.php/craiaj> & <http://www.craiaj.info/>

- functional theory study. *Chemical Engineering Science*, 135, 403-411. <https://doi.org/10.1016/j.ces.2015.01.068>
- Francis, A. W., & Reid, E. E. (1946). Ethylbenzene. *Industrial & Engineering Chemistry*, 38(11), 1194-1203. <https://doi.org/10.1021/ie50443a023>
- Gauli, H. R. K., Rai, K. B., Giri, K. & Neupane, R. (2023). Monte-Carlo simulation of phase transition in 2d and 3d Ising model. *Scientific World*. 16(16): 12-20. [doi.org/10.3126/sw.v16i16.56744](https://doi.org/10.3126/sw.v16i16.56744)
- Joshi, B. D., Tandon, P., & Jain, S. (2013). Structure, MESP and HOMO-LUMO study of 10-Acetyl-10H-phenothiazin e5-oxide using vibrational spectroscopy and quantum chemical methods. *BIBECHANA*, 9, 38-49.
- Kenouche, S., Sandoval-Yañez, C., & Martínez-Araya, J. I. (2022). The antioxidant capacity of myricetin. A molecular electrostatic potential analysis based on DFT calculations. *Chemical Physics Letters*, 801, 139708. <https://doi.org/10.1016/j.cplett.2022.139708>
- Khadka, I. B., Rai, K. B., Alsardia, M. M., Haq, B. U., & Kim, S. H. (2023). Raman investigation of substrate-induced strain in epitaxially grown graphene on low/high miscut angled silicon carbide and its application perspectives. *Optical Materials*, 140, 113836. [doi.org/10.1016/j.optmat.2023.113836](https://doi.org/10.1016/j.optmat.2023.113836)
- Khalili, F., Vafae, M., Cho, D., & Shokri, B. (2021). Charge migration in caffeine: A real time time dependent density functional theory study. *International Journal of Quantum Chemistry*, 121(19), e26754. <https://doi.org/10.1002/qua.26754>
- Limbu, S., Ojha, T., Ghimire, R. R. & Rai, K. B. (2024). An investigation of vibrational analysis, thermodynamics properties and electronic properties of Formaldehyde and its stretch by substituent acetone, acetyl chloride and methyl acetate using First Principles analysis. *BIBECHANA*, 21(1), 23–36. <https://doi.org/10.3126/bibechana.v21i1.58684>
- Ludwig, V., Ludwig, Z. M. D. C., Rodrigues, M. M., Anjos, V., Costa, C. B., Das Dores, D. R. S. A., Silva, V. R., Soares, F. (2018). Analysis by Raman and infrared spectroscopy combined with theoretical studies on the identification of plasticizer in PVC films. *Vibrational Spectroscopy*, 98, 134-138. <https://doi.org/10.1016/j.vibspec.2018.08.004>

- Noei, M., Ahmadaghaei, N., & Salari, A. A. (2017). Ethyl benzene detection by BN nanotube: DFT studies. *Journal of Saudi chemical society*, 21, S12-S16. <https://doi.org/10.1016/j.jscs.2013.09.008>
- O'boyle, N. M., Tenderholt, A. L., & Langner, K. M. (2008). CcLib: a library for package independent computational chemistry algorithms. *Journal of computational chemistry*, 29(5), 839-845. <https://doi.org/10.1002/jcc.20823>
- Ojha, T., Limbu, S., Shrestha, P. M., Gupta, S. P. & Rai, K. B. (2023). Comparative Computational Study on Molecular Structure, Electronic and Vibrational Analysis of Vinyl Bromide based on HF and DFT Approach. *Himalayan Journal of Science and Technology*, 7(1), 38-49. <https://doi.org/10.3126/hijost.v7i1.61128>
- Rai, K. B., Ghimire, R. R., Dhakal, C., Pudasainee, K. & Siwakoti, B. (2024). Structural Equilibrium Configuration of Benzene and Aniline: A First-Principles Study. *Journal of Nepal Chemical Society*. 44(1), 1-15. <https://doi.org/10.3126/jncs.v44i1.62675>
- Rai, K. B., Khadka, I. B., Koirala, A. R. & Ray, S. C. (2021). Insight of cleaning, doping and defective effects on the graphene surface by using methanol. *Advances in Materials Research*, 10(4), 283-292. <https://doi.org/10.12989/amr.2021.10.4.283>
- Rijal, R., Lamichhane, H. P., & Pudasainee, K. (2022). Molecular structure, HOMO-LUMO analysis and vibrational spectroscopy of the cancer healing pro-drug temozolomide based on DFT calculations. *AIMS Biophysics*, 9(3), 208–220. DOI: [10.3934/biophy.2022018](https://doi.org/10.3934/biophy.2022018)
- Sangeetha, R., Seshadri, S., & MP, R. (2017). Vibrational spectroscopic (FT-IR and Ft-Raman) studies, Uv, NMR and HOMO-LUMO analysis of 2-bromo-1-fluoro-4-nitrobenzene. *International Journal of Advance Engineering and Research Development*, 4(8), 279-294.
- Sharma, S. K., Verma, D. S., Khan, L. U., Kumar, S., & Khan, S. B. (Eds.). (2018). *Handbook of materials characterization*. New York, NY, USA: Springer International Publishing.
- Shin, H. C., Ahn, S. J., Kim, H. W., Moon, Y., Rai, K. B., Woo, S. H. & Ahn, J. R. (2016). Room temperature deintercalation of alkali metal atoms from epitaxial graphene by formation of charge-transfer complexes. *Applied Physics Letter*, 109, 081603. <https://doi.org/10.1063/1.4961633>

- Wang, W., Qiu, X., Wang, Y., Zhang, S. & Zhang, B. (2012). Vibrational Spectra and Quantum Calculations of Ethylbenzene. *Chinese Journal of Chemical Physics*, 25(5), 526-532. DOI:10.1088/1674-0068/25/05/526-532
- Zhou, Z., Zhang, X., Liu, Y., & Abulimiti, B. (2022). Study on physical properties of ethylbenzene under external electric field. *Computational and Theoretical Chemistry*, 1207, 113533. <https://doi.org/10.1016/j.comptc.2021.113533>