

A DFT STUDY ON SUBSTITUENT EFFECTS ON IRON CORROSION INHIBITION CAPABILITY OF INDOLE DERIVATIVES

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Abstract - The corrosion inhibition activity of indole derivatives has been systematically examined by calculating quantum chemical parameters including energy of the highest occupied molecular orbital, energy of the lowest unoccupied molecular orbital, energy difference, molecular hardness, molecular softness, and the number of electrons exchanged between the metal and the corrosion inhibitor at the B3LYP/6-311++G (d,p) level of theory. The results demonstrate that derivatives containing the electron-donating groups exhibit superior efficiency in inhibiting iron corrosion compared to indole. Additionally, an investigation into the corrosion inhibition ability of derivatives containing the NH₂ group reveals that 6-NH₂-indole emerges as the most effective inhibitor, boasting an efficiency value of 97.11%. These calculated outcomes align with previously studied experimental results, underscoring the remarkable corrosion resistance of derivatives containing electron-donating groups.

Key words - Indole derivatives; inhibitors; quantum calculation; electron-donating group; corrosion.

1. Introduction

Metal corrosion poses a significant and global concern for scientists, prompting the exploration of effective measures to safeguard metal surfaces [1, 2]. Among various approaches, the utilization of organic compounds as metal corrosion inhibitors has garnered attention due to their ease of synthesis, cost-effectiveness, and environmental safety [3]. The investigation of metal corrosion inhibitors can be carried out through experimental or theoretical methods. Experimental techniques such as gravimetric analysis, polarization curve measurements, and impedance spectroscopy are commonly employed. However, these methods often demand substantial resources and time to choose a new corrosion inhibitor among many investigated compounds. Conversely, the application of computational chemistry, mainly through the utilization of density functional theory (DFT), has significantly advanced this approach in designing and developing organic corrosion inhibitors [4]. DFT has empowered corrosion scientists to make precise predictions regarding the inhibition efficiencies of organic corrosion inhibitors by leveraging electronic/molecular properties and reactivity indices [5]. The study employs the B3LYP density functional theory, coupled with the 6-311++G(d,p) basis set.

Indole, a heterocyclic compound featuring a benzene and pyrrole ring, is renowned for its corrosion-inhibiting characteristics [6]. Its distinctive structure, characterized by an aromatic and heterocyclic ring system with lone electrons, facilitates adsorption on metal surfaces [7, 8]. In addition, numerous studies have indicated that the presence

of electron-donating groups, such as -OH, -NH₂, -N(CH₃)₂, -CH₃, -OCH₃, etc., enhances inhibition efficiency, whereas electron-withdrawing groups like -NO₂, -CN, -COOC₂H₅ diminish the inhibition efficiency of organic molecules [9, 10]. Electronic substituents contribute to heightened electron density at the absorption center of the inhibitor, thereby augmenting the interaction between the inhibitor molecule and the metal surface [11, 12]. Consequently, this study examines the impact of electron-donating groups on the iron corrosion inhibition potential of indole compounds. The utilization of Density Functional Theory (DFT) is proposed to elucidate the electron configuration of the derivatives to establish a correlation between molecular structure and inhibition efficiency. The research outcomes are anticipated to yield valuable insights for the design and synthesis of novel inhibitors with enhanced efficiency. All computational analyses will be executed using Gaussian 16 software [13].

2. Methods

The quantum chemical calculations based on DFT at 6-311G++ (d,p) basis set were used because this basis set is very popular for determining the electronic and molecular geometry accurately. According to convergency tests, at least triple-zeta basis set augmented with polarization and diffuse functions should be used to obtain converged results that compare well with the results obtained from plane-wave calculations [14].

Quantum chemical parameters crucial for probing the corrosion inhibition potential of an organic compound encompass the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the LUMO-HOMO energy difference ($\Delta E_{\text{L-H}}$), molecular hardness (η), molecular softness (S), and the number of electrons exchanged between the metal and the corrosion inhibitor (ΔN). A higher E_{HOMO} value signifies increased electron donation capability, while a smaller E_{LUMO} value indicates enhanced electron acceptance ease [15].

The $\Delta E_{\text{L-H}}$ value, derived from E_{HOMO} and E_{LUMO} using formula (1), serves as an indicator of molecular polarity. The larger values of $\Delta E_{\text{L-H}}$ denote less polar molecules.

$$\Delta E_{\text{L-H}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

Koopmans' DFT theorem facilitates the calculation of first ionization energy (IE) and electron affinity (EA) using formulas (2) and (3), respectively.

$$\text{IE} = -E_{\text{HOMO}} \quad (2)$$

$$EA = -E_{LUMO} \quad (3)$$

Molecular hardness (η) reflects molecular strength, while molecular softness (S) assesses molecular polarity. Larger η and smaller S values denote greater molecular stability and reduced propensity for chemical interactions [16], calculated through formulas (4) and (5).

$$\eta = \frac{IE - EA}{2} = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (4)$$

$$S = \frac{1}{\eta} \quad (5)$$

Additionally, the corrosion inhibition evaluation involves absolute electron affinity (χ), approximated by formula (6) [17].

$$\chi = \frac{IE + EA}{2} = -\frac{(E_{HOMO} + E_{LUMO})}{2} \quad (6)$$

During the adsorption process on the metal surface, the electron exchange between an inhibitor molecule and metal surface (ΔN) is determined by formula (7), where χ , η , and Φ represent absolute electron affinity, hardness, and work function, respectively [18].

$$\Delta N = \frac{\Phi - \chi_{inh}}{2(\eta_M + \eta_{inh})} \quad (7)$$

Regarding Φ , its value is 4.82 eV corresponding to the Fe (110) surface [19].

The theoretical corrosion inhibition performance of indole derivatives is calculated using formulas (8), (9), and (10) [20].

$$IE_{add} \% = \frac{IE_{Indole} - IE_{X-Indole}}{IE_{Indole}} \times 100 \quad (8)$$

$$H_{add} \% = \frac{IE_{add} \% \times H_{ex} \%}{100} \quad (9)$$

$$H_{theo} \% = H_{add} \% + H_{ex} \% \quad (10)$$

Here, $IE_{add}\%$, $H_{theo}\%$, $H_{ex}\%$, and $H_{add}\%$ denote the ionization potential percentage of the additive, theoretically calculated inhibition efficiency percentage of indole derivatives, experimental inhibition efficiency of indole, and inhibition efficiency percentage of the additive, respectively. IE_{indole} and $IE_{X-indole}$ represent the ionization energies of indole and X-indole derivatives, computed using equation (2).

3. Results and Discussion

3.1. Optimization of the geometry of indole

The molecular geometry of indole inhibitor subjects to optimization through theoretical calculations at the B3LYP/6-311++G(d,p) level of theory, as depicted in Figure 1.

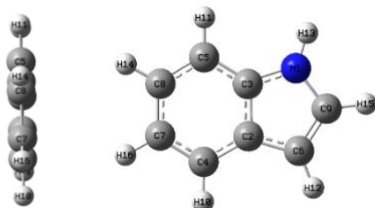


Figure 1. Optimized geometry of indole at B3LYP/6-311++G(d,p)

The impeccably planar structure exhibited by indole underscores its capability to provide effective coverage when adsorbed onto metal surfaces. This structural characteristic enhances its potential to shield the metal surface from corrosive agents in solution, thereby contributing to corrosion protection.

The highest occupied molecular orbital (HOMO) serves as an indicator of the electron-donating positions within the corrosion inhibitor molecule [21], while the lowest unoccupied molecular orbital (LUMO) signifies the molecule's electron-accepting capacity [22]. Consequently, both the HOMO and LUMO of indole are scrutinized, as depicted in Figure 2. Notably, Figure 2 reveals a widespread distribution of electron donor and acceptor positions throughout the indole molecule.

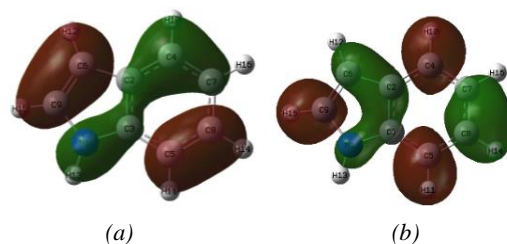


Figure 2. (a) HOMO and (b) LUMO of indole

3.2. Corrosion inhibition assessment of NH₂-indole derivatives through quantum chemical parameters

Figure 3 illustrates the configurations of derivatives featuring NH₂ group positioned at various sites within indole molecule. These compounds serve as representatives of indole derivatives containing electron-donating groups. The optimization of these structures is carried out using the B3LYP/6-311++G(d,p) theoretical approach.

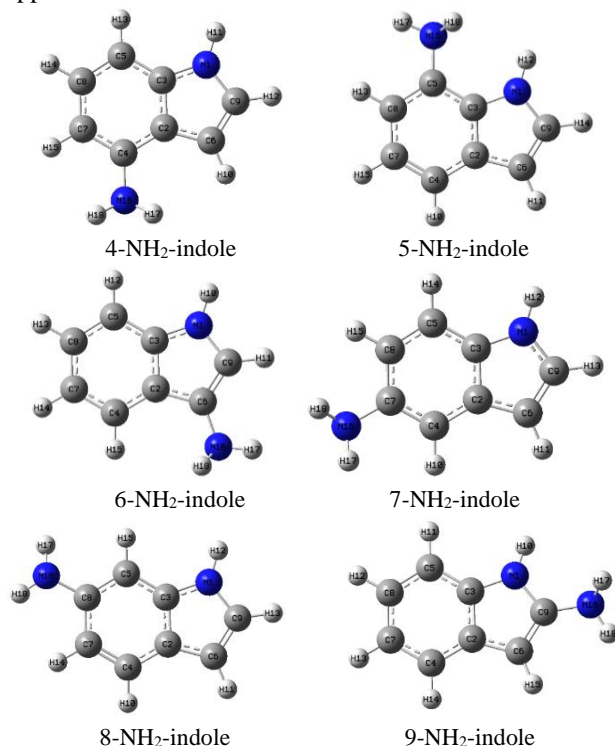


Figure 3. Optimized geometry of NH₂-indole derivatives at B3LYP/6-311++G(d,p)

The stability and adsorption characteristics of the inhibitor molecule are significantly influenced by both the structure and position of the substituent group. Consequently, an investigation is undertaken into the structural parameters of indole and its derivatives containing NH₂ group at different positions. The bond lengths and molecular angles are detailed in Table S1. The bond lengths and bond angles of derivatives containing the NH₂ group generally exhibit negligible variations when compared to those of indole. Results indicate that indole adopts a perfectly planar geometry, while derivatives containing the NH₂ group exhibit near coplanarity with the indole ring, as evidenced by dihedral angles such as C8-C7-C4-N16, C7-C8-C5-N16, N1-C9-C6-N16, C2-C4-C7-N16, C3-C5-C8-N16, and C3-N1-C9-N16, with corresponding values of 177.07°, 177.98°, 175.89°, 176.84°, 176.97°, and 175.36° for 4-NH₂-indole, 5-NH₂-indole, 6-NH₂-indole, 7-NH₂-indole, 8-NH₂-indole, and 9-NH₂-indole, respectively. This structural configuration suggests that both indole and NH₂-indole derivatives hold promise as compounds capable of forming effective coverage when adsorbed onto metal surfaces.

Determining atomic charges is conducted utilizing the natural population analysis method, and the ensuing outcomes are outlined in Table 1. Notably, the nitrogen atom N1 within the indole ring and the N16 atom within the NH₂ groups exhibit the highest negative charges. Furthermore, it is noteworthy that, across all compounds, the atoms constituting the aromatic ring framework consistently manifest negative charges (except C2). This observation implies that these specific atoms serve as negative charge centers, capable of furnishing electrons (nucleophilic centers) to the unoccupied d orbitals of the iron surface.

Table 1. Atomic charges for NH₂-indole derivatives at B3LYP/6-311++G(d,p)

Atoms	4-NH ₂ -indole	5-NH ₂ -indole	6-NH ₂ -indole	7-NH ₂ -indole	8-NH ₂ -indole	9-NH ₂ -indole
N1	-0.08	-0.12	-0.11	-0.09	-0.09	-0.15
C2	1.56	0.90	0.98	1.71	1.95	1.83
C3	0.04	-0.34	-0.19	-1.01	-1.03	-1.18
C4	-1.24	-0.98	-0.65	-0.62	-0.94	-0.75
C5	-0.73	-0.73	-0.56	-0.70	-0.27	-0.49
C6	-0.17	0.38	0.21	-0.19	-0.36	0.10
C7	-0.32	-0.23	-0.50	-0.45	0.31	0.04
C8	-0.14	0.22	-0.12	0.17	-0.79	-0.42
C9	-0.10	-0.23	-0.19	-0.02	0.04	-0.13
N16	-0.30	-0.37	-0.38	-0.31	-0.29	-0.36

Quantum chemical parameters are numerical values derived from quantum mechanical calculations that describe various aspects of the electronic structure and behavior of molecules. These parameters provide insights into the energetics, stability, and reactivity of molecules at the molecular level [23]. E_{HOMO} and E_{LUMO} serve as crucial parameters in assessing corrosion inhibition ability. E_{HOMO} represents the energy of the highest occupied molecular orbital, while E_{LUMO} indicates the energy of the lowest unoccupied molecular orbital. A

greater E_{HOMO} value signifies an enhanced capacity of the molecules to donate electrons [24]. As can be seen in Table 2, the E_{HOMO} of indole is recorded at -5.8 eV. In the presence of the NH₂ group, these values exhibit an increase. Specifically, E_{HOMO} values of -5.16, -5.41, -5.13, -5.23, -5.14, and -5.34 eV correspond to 4-NH₂-indole, 5-NH₂-indole, 6-NH₂-indole, 7-NH₂-indole, 8-NH₂-indole, and 9-NH₂-indole, respectively. Notably, 6-NH₂-indole demonstrates the highest electron-donating capability with most significant value of E_{HOMO} among NH₂ group-containing derivatives.

Upon scrutinizing the E_{LUMO} values, it becomes evident that indole possesses the lowest E_{LUMO} value (-0.62 eV) in comparison to NH₂-indole derivatives (-0.58 ÷ -0.37 eV). This signifies that indole exhibits a higher propensity to accept electrons when contrasted with its NH₂-containing derivatives.

Moreover, the efficiency of a substance in inhibiting metal corrosion is further appraised through its capacity for adsorption onto the iron surface. Consequently, the more polar the studied molecule, the more facile its adsorption onto the metal surface, enhancing its effectiveness in corrosion inhibition. The theoretical perspectives outlined in the research methods section posit that substances exhibiting robust corrosion inhibition possess low ΔE_{L-H} and η values coupled with high S [25]. According to the calculated data at B3LYP/6-311++G(d,p), as presented in Table 2, 6-NH₂-indole emerges as the most polarizable compound, with ΔE_{L-H}, η, and S values of 4.55 eV, 2.27 eV, and 0.44 eV⁻¹, respectively. The order of iron corrosion inhibition, evaluated based on ΔE_{L-H}, η, and S, is organized as follows: 6-NH₂-indole > 7-NH₂-indole > 8-NH₂-indole > 9-NH₂-indole > 4-NH₂-indole > 5-NH₂-indole.

Table 2. Quantum chemical parameters of indole and NH₂-indole derivatives

Comp-ounds	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	H (eV)	S (eV ⁻¹)	ΔN
Indole	-5.80	-0.62	5.18	2.59	0.39	0.31
4-NH ₂ -indole	-5.16	-0.37	4.79	2.40	0.42	0.43
5-NH ₂ -indole	-5.41	-0.55	4.86	2.43	0.41	0.38
6-NH ₂ -indole	-5.13	-0.58	4.55	2.27	0.44	0.43
7-NH ₂ -indole	-5.23	-0.53	4.71	2.35	0.43	0.41
8-NH ₂ -indole	-5.14	-0.42	4.72	2.36	0.42	0.43
9-NH ₂ -indole	-5.34	-0.57	4.77	2.38	0.42	0.39

In assessing the potential for electron exchange between the inhibitor molecule and the Fe(110) surface, the quantity ΔN is crucial for calculation. As indicated in Table 2, both indole and NH₂-indole exhibit ΔN values ranging from 0.31 to 0.43. According to Lukovits's research [26], when ΔN < 3.6, the inhibition efficiency tends to increase, signifying the enhanced ability of the inhibitor to donate electrons at the metal surface. All NH₂-indole derivatives satisfy these conditions, demonstrating a superior capacity for electron exchange with the Fe(110) surface compared to indole.

The comprehensive assessment of quantum chemical parameters consistently designates 6-NH₂-indole as the substance exhibiting the most effective ability to inhibit

iron corrosion. Consequently, this compound is selected for further in-depth research.

3.3. Effects of electron-donating substituent groups on iron corrosion inhibition ability of indole derivatives

The examined derivatives of indole featuring electron-donating groups encompass 6-OH-indole, 6-CH₃O-indole, 6-N(CH₃)₂-indole, and 6-CH₃-indole. The optimized structures of these derivatives are illustrated in Figure 4. The effectiveness of these compounds in inhibiting iron corrosion is systematically assessed and compared to the inhibitory performance of 6-NH₂-indole.

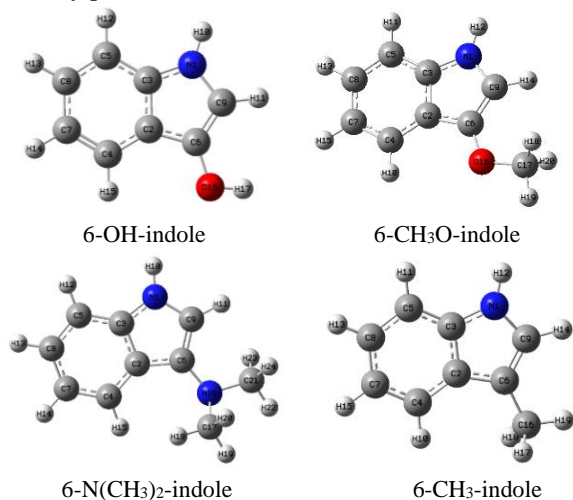


Figure 4. Optimized geometry of indole derivatives containing electron-donating groups at B3LYP/6-311++G(d,p)

Upon comparing the quantization parameter values of indole and its derivatives featuring electron-donating groups, a consistent trend emerges, marked by an elevation in E_{HOMO} values as delineated in Table 3. Notably, 6-NH₂-indole exhibits the highest E_{HOMO} value, establishing itself as the most effective electron donor among the derivatives with electron-donating groups. In terms of E_{LUMO} value, 6-OH-indole stands out as the substance with the most pronounced inclination to accept electrons. An essential metric in assessing the capacity of inhibitor molecules to interact with metal surfaces is the ΔE value, which consistently decreases in the presence of electron-donating groups in the indole molecule (ranging from 5.04 to 4.55 eV). 6-NH₂-indole, with the smallest ΔE value (4.55 eV), emerges as the most polar molecule, substantiating its superior reactivity.

Table 3. Quantum chemical parameters of indole derivatives containing electron-donating groups

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	H (eV)	S (eV ⁻¹)	ΔN
6-OH-indole	-5.42	-0.64	4.78	2.39	0.42	0.37
6-N(CH ₃) ₂ -indole	-5.14	-0.57	4.57	2.28	0.44	0.42
6-CH ₃ -indole	-5.63	-0.58	5.04	2.52	0.40	0.34
6-CH ₃ O-indole	-5.36	-0.58	4.79	2.39	0.42	0.39

The η values follow the same decreasing trend as ΔE , ranging from 2.52 to 2.27. In contrast to molecular hardness, the molecular softness of these derivatives (S)

increases from 0.40 to 0.44 eV⁻¹, indicative of their enhanced ability to react with iron compared to indole. This is further supported by the derivatives' elevated electron exchange numbers compared to indole (0.31), with 6-NH₂-indole (0.43) as the entity with superior electron exchange capability among the investigated derivatives.

3.4. Theoretical calculation of iron corrosion inhibition efficiency in indole derivatives

Table 4. Theoretical calculation of iron corrosion inhibition efficiency in indole derivatives

	IE	IE _{add} %	H _{add} %	H _{ex} %	H _{theo} %
Indole	5.80	0.00	0.00	87.00	87.00
6-OH-indole	5.42	6.52	5.67		92.67
6-N(CH ₃) ₂ -indole	5.14	11.40	9.92		96.92
6-NH ₂ -indole	5.13	11.62	10.11		97.11
6-CH ₃ -indole	5.63	3.00	2.61		89.61
6-CH ₃ O-indole	5.36	7.53	6.55		93.55

Indole demonstrates a remarkable capacity to inhibit steel corrosion in a 1.0 M HCl acid medium, exhibiting inhibition efficiencies of 87.00% via impedance spectroscopy and 88.00% via the mass method [27]. Leveraging the experimental performance data of indole, along with the formulas (8), (9), and (10), the corrosion inhibition effectiveness of indole derivatives is subsequently theoretically calculated and presented in Table 4. Specifically, 6-OH-indole, 6-N(CH₃)₂-indole, 6-NH₂-indole, 6-CH₃-indole, and 6-CH₃O-indole manifest inhibition efficiency values of 92.67%, 96.92%, 97.11%, 89.61%, and 93.55%, respectively. Consequently, 6-NH₂-indole emerges as the most effective iron corrosion inhibitor among the surveyed indole derivatives. This theoretical finding aligns with experimental observations regarding the robust steel corrosion inhibition ability of indole derivatives containing the NH₂ group [28].

4. Conclusion

Computational investigation utilizing density functional theory at the B3LYP/6-311++G(d,p) level of theory was conducted to correlate inhibition efficiency and electronic properties/molecular structures of indole derivatives used as corrosion inhibitors. The outcomes reveal that all quantum chemical parameters, including the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the LUMO–HOMO energy difference ($\Delta E_{\text{L-H}}$), molecular hardness (η), molecular softness (S), and the number of electrons exchanged between the metal and inhibitor (ΔN), consistently indicate that derivatives containing electron-donating groups, such as 6-OH-indole, 6-N(CH₃)₂-indole, 6-NH₂-indole, 6-CH₃-indole, 6-CH₃O-indole, exhibit superior performance as metal corrosion inhibitors compared to indole. Among these, 6-NH₂-indole stands out for displaying the highest corrosion inhibition ability. Notably, these research findings align with certain published experimental results. The insights derived from this theoretical research endeavor hold potential significance in guiding the selection of prospective corrosion inhibitors in future applications.

Declaration of Competing Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX

Table S1. Some structural parameters of indole and NH₂-indole derivatives at B3LYP/6-311++G(d,p)

Compounds	Indole	4-NH ₂ -indole	5-NH ₂ -indole	6-NH ₂ -indole	7-NH ₂ -indole	8-NH ₂ -indole	9-NH ₂ -indole
Bond lengths (Å)							
N1-C3	1.38	1.38	1.38	1.37	1.39	1.38	1.39
C3-C5	1.40	1.40	1.40	1.40	1.39	1.40	1.39
C5-C8	1.39	1.39	1.39	1.39	1.39	1.39	1.39
C8-C7	1.41	1.41	1.41	1.41	1.42	1.42	1.40
C7-C4	1.39	1.39	1.38	1.39	1.39	1.38	1.39
C4-C2	1.40	1.41	1.41	1.40	1.40	1.40	1.40
C2-C3	1.42	1.42	1.42	1.42	1.42	1.42	1.42
C2-C6	1.44	1.44	1.44	1.44	1.44	1.44	1.44
C6-C9	1.37	1.37	1.37	1.37	1.37	1.37	1.37
C9-N1	1.38	1.38	1.38	1.39	1.38	1.39	1.38
C4-N16		1.40					
C5-N16			1.41				
C6-N16				1.41			
C7-N16					1.41		
C8-N16						1.40	
C9-N16							1.40
Bond angles (°)							
N1-C3-C5	130.57	130.19	129.36	130.79	131.08	130.14	130.31
C3-C5-C8	117.52	116.53	116.50	117.73	118.06	117.99	117.60
C5-C8-C7	121.20	121.94	121.47	121.31	121.66	119.93	120.91

C8-C7-C4	121.12	121.50	121.68	120.93	119.86	121.57	121.20
C7-C4-C2	119.09	117.88	118.28	119.00	119.55	119.65	119.14
C4-C2-C6	134.29	133.60	134.27	133.71	133.91	134.86	134.28
C2-C6-C9	107.13	107.05	107.36	106.98	107.20	107.17	107.03
C6-C9-N1	109.52	109.26	109.56	109.31	109.59	109.28	109.72
C9-N1-C3	109.29	109.64	108.74	109.22	109.07	109.41	108.97
N1-C3-C2	107.15	106.88	107.80	107.45	107.36	107.10	107.16

Table S2. Optimized structure of indole and its derivatives in gas phase using B3LYP/6-311++G(d,p).

Stable Neutral form (indole)	C ₈ H ₇ N	
0 1		
N	-1.56592200	-1.08030300
C	-0.24856400	0.74926900
C	-0.24725400	-0.67192300
C	0.98158100	1.42718900
C	0.93476100	-1.41687600
C	-1.62386700	1.16574600
C	2.15665500	0.69135400
C	2.13356300	-0.71737300
C	-2.38851500	0.03132600
H	1.01052500	2.51137600
H	0.92016700	-2.50142500
H	-1.99694200	2.17793900
H	-1.88172800	-2.03529200
H	3.06932000	-1.26468500
H	-3.46128400	-0.08199200
H	3.11123900	1.20392800
Zero-point correction= 0.129095 (Hartree/Particle)		
Thermal correction to Energy= 0.135445		
Thermal correction to Enthalpy= 0.136389		
Thermal correction to Gibbs Free Energy= 0.098744		
Sum of electronic and zero-point Energies= -363.784892		
Sum of electronic and thermal Energies= -363.778543		
Sum of electronic and thermal Enthalpies= -363.777599		
Sum of electronic and thermal Free Energies= -363.815244		
Stable Neutral form (4-NH ₂ -Indole)	4-NH ₂ -C ₈ H ₆ N	
0 1		
N	2.09425700	0.66374300
C	0.18026100	-0.51333700
C	0.72005700	0.79647100
C	-1.22258700	-0.68134700
C	-0.07634700	1.94781300
C	1.28873100	-1.42931400
C	-2.01640900	0.46483900
C	-1.44906500	1.75132100
C	2.43146300	-0.67655000
H	1.25571400	-2.50727400
H	2.74990100	1.42649100
H	3.46524100	-0.98387200
H	0.35406800	2.94217900
H	-2.10975000	2.61113500
H	-3.09684000	0.36142800
N	-1.77871800	-1.96239800
H	-1.21902800	-2.69633900
H	-2.74470700	-2.02254600
Zero-point correction= 0.145724 (Hartree/Particle)		
Thermal correction to Energy= 0.153574		
Thermal correction to Enthalpy= 0.154518		
Thermal correction to Gibbs Free Energy= 0.113756		
Sum of electronic and zero-point Energies= -419.144721		

Sum of electronic and thermal Energies= -419.136872		
Sum of electronic and thermal Enthalpies= -419.135927		
Sum of electronic and thermal Free Energies= -419.176690		
Stable Neutral form (5-NH ₂ -indole)	5-NH ₂ -C ₈ H ₆ N	
0 1		
N	1.27912400	-1.30078200
C	0.72120300	0.89067900
C	0.20612600	-0.42735500
C	-0.17297300	1.97720300
C	-1.16861300	-0.70697900
C	2.15423000	0.76984600
C	-1.53114100	1.70908900
C	-2.02515800	0.38931600
C	2.45113300	-0.56502000
H	0.19265800	2.99728900
H	2.87210100	1.57491100
H	1.21757200	-2.28255200
H	-3.09764500	0.22119500
H	3.40811400	-1.06220800
H	-2.24087900	2.52874500
N	-1.61390100	-2.04673900
H	-2.62124000	-2.12956600
H	-1.19608000	-2.63583700
Zero-point correction= 0.145889 (Hartree/Particle)		
Thermal correction to Energy= 0.153713		
Thermal correction to Enthalpy= 0.154657		
Thermal correction to Gibbs Free Energy= 0.113888		
Sum of electronic and zero-point Energies= -419.141875		
Sum of electronic and thermal Energies= -419.134051		
Sum of electronic and thermal Enthalpies= -419.133107		
Sum of electronic and thermal Free Energies= -419.173875		
Stable Neutral form (6-NH ₂ -indole)	6-NH ₂ -C ₈ H ₆ N	
0 1		
N	0.70115700	1.78285500
C	0.17160000	-0.40764000
C	-0.36005400	0.91059700
C	-0.70737400	-1.50194600
C	-1.73755500	1.14838800
C	1.60593800	-0.28377200
C	-2.07430700	-1.26658300
C	-2.58302300	0.04752500
C	1.89203700	1.05718300
H	0.63649400	2.78568100
H	2.84522800	1.56204100
H	-2.13479200	2.15767000
H	-3.65612600	0.20180100
H	-2.76457400	-2.10227400
H	-0.32611300	-2.51700900
N	2.50168100	-1.36736500
H	3.46806200	-1.10002800
H	2.26838000	-2.11881600
Zero-point correction= 0.145385 (Hartree/Particle)		
Thermal correction to Energy= 0.153566		
Thermal correction to Enthalpy= 0.154510		
Thermal correction to Gibbs Free Energy= 0.112890		
Sum of electronic and zero-point Energies= -419.137271		
Sum of electronic and thermal Energies= -419.129090		
Sum of electronic and thermal Enthalpies= -419.128146		
Sum of electronic and thermal Free Energies= -419.169766		
Stable Neutral form (7-NH ₂ -indole)	7-NH ₂ -C ₈ H ₆ N	
0 1		

N	2.18721700	0.83389900	0.00688700
C	0.52521700	-0.69597600	-0.00318400
C	0.80931800	0.69369000	0.00102000
C	-0.81254500	-1.12450000	-0.00533800
C	-0.20902000	1.64697400	0.00025100
C	1.78955900	-1.37767100	0.00000400
C	-1.83552900	-0.18104000	-0.00711500
C	-1.52117100	1.19949400	-0.00686800
C	2.76755000	-0.41755600	0.00554000
H	-1.04850400	-2.18414600	-0.01068600
H	1.95421200	-2.44386400	-0.00247000
H	2.68731900	1.70617400	0.00727100
H	3.84113900	-0.52389700	0.00793600
H	0.00766000	2.70978200	0.00265300
H	-2.33053300	1.92213600	-0.02045000
N	-3.18650700	-0.57722700	-0.07596100
H	-3.36179800	-1.51756100	0.24945900
H	-3.83474500	0.07417500	0.34394500
Zero-point correction= 0.145328 (Hartree/Particle)			
Thermal correction to Energy= 0.153313			
Thermal correction to Enthalpy= 0.154258			
Thermal correction to Gibbs Free Energy= 0.113176			
Sum of electronic and zero-point Energies= -419.141555			
Sum of electronic and thermal Energies= -419.133570			
Sum of electronic and thermal Enthalpies= -419.132625			
Sum of electronic and thermal Free Energies= -419.173707			
Stable Neutral form (8-NH₂-indole)		8-NH₂-C₈H₆N	
0 1			
N	1.73177800	-1.29108300	0.00035600
C	0.82960200	0.77061600	0.00164300
C	0.52960200	-0.61640100	-0.00270500
C	-0.24059400	1.67818800	0.00044600
C	-0.77882000	-1.10712200	-0.00563000
C	2.26280700	0.89199600	0.00686400
C	-1.54062500	1.20377100	-0.00558300
C	-1.82359400	-0.18443500	-0.00685000
C	2.77499400	-0.37485100	0.00501200
H	-0.05584700	2.74699200	0.00353800
H	2.83786900	1.80485100	0.01095700
H	1.83993400	-2.29084900	-0.00878400
H	3.79921200	-0.71248400	0.00648600
H	-2.36927600	1.90456600	-0.01589000
H	-0.98238400	-2.17329200	-0.01420200
N	-3.15921500	-0.61478900	-0.07359500
H	-3.32498100	-1.54873400	0.27318100
H	-3.83269300	0.03948000	0.29821000
Zero-point correction= 0.145387 (Hartree/Particle)			
Thermal correction to Energy= 0.153326			
Thermal correction to Enthalpy= 0.154271			
Thermal correction to Gibbs Free Energy= 0.113306			
Sum of electronic and zero-point Energies= -419.142693			
Sum of electronic and thermal Energies= -419.134754			
Sum of electronic and thermal Enthalpies= -419.133809			
Sum of electronic and thermal Free Energies= -419.174774			
Stable Neutral form (9-NH₂-indole)		9-NH₂-C₈H₆N	
0 1			
N	-1.13902500	-1.05179600	0.02495900
C	0.21290500	0.76113300	-0.00027600
C	0.19471800	-0.65869100	0.00288600
C	1.45191700	1.41679300	0.00615300
C	1.35815100	-1.42194800	0.00065300

C	-1.15743200	1.20183200	0.00585400
C	2.61858400	0.65988600	0.00099100
C	2.57497300	-0.74386900	-0.00578800
C	-1.94126800	0.07651400	-0.00009900
H	-1.47102100	-1.97071300	-0.22010900
H	1.32315500	-2.50614300	0.00399500
H	3.50006900	-1.30868900	-0.01348500
H	3.58059600	1.16010200	0.00159900
H	1.50025900	2.50034100	0.01113500
H	-1.51499900	2.21945400	0.03942500
N	-3.32620900	-0.08621400	-0.08322300
H	-3.71729300	-0.67334700	0.64485500
H	-3.81941400	0.79516200	-0.12180300
Zero-point correction= 0.145720 (Hartree/Particle)			
Thermal correction to Energy= 0.153587			
Thermal correction to Enthalpy= 0.154531			
Thermal correction to Gibbs Free Energy= 0.113652			
Sum of electronic and zero-point Energies= -419.143666			
Sum of electronic and thermal Enthalpies= -419.134854			
Sum of electronic and thermal Free Energies= -419.175734			
Stable Neutral form (6-OH-indole)		6-OH-C₈H₆N	
0 1			
N	-0.75387500	1.75257800	0.00000100
C	-0.16369700	-0.42611200	0.00000100
C	0.32984500	0.90597800	0.00000000
C	0.73860600	-1.50102300	0.00000100
C	1.70150900	1.17887500	-0.00000100
C	-1.59304100	-0.32792800	0.00000200
C	2.09751400	-1.22874000	0.00000000
C	2.57265400	0.09908900	-0.00000200
C	-1.92774900	0.99987000	0.00000200
H	-0.71412000	2.75679600	-0.00000300
H	-2.89517900	1.47667800	0.00000600
H	2.07341900	2.19771900	-0.00000200
H	3.64159700	0.28006800	-0.00000300
H	2.80989400	-2.04570300	0.00000000
H	0.37254900	-2.52086500	0.00000300
O	-2.40237900	-1.43141900	0.00000600
H	-3.32585200	-1.16144500	-0.00006900
Zero-point correction= 0.132558 (Hartree/Particle)			
Thermal correction to Energy= 0.140719			
Thermal correction to Enthalpy= 0.141663			
Thermal correction to Gibbs Free Energy= 0.099847			
Sum of electronic and zero-point Energies= -439.019569			
Sum of electronic and thermal Energies= -439.011408			
Sum of electronic and thermal Enthalpies= -439.010464			
Sum of electronic and thermal Free Energies= -439.052280			
Stable Neutral form (6-CH₃O-indole)		6-CH₃O-C₈H₆N	
0 1			
N	-0.06255800	1.90168400	0.00037300
C	0.19642200	-0.33976300	0.00002200
C	0.88271100	0.90276100	0.00014900
C	0.92716000	-1.53699700	-0.00018300
C	2.27971300	0.96752000	0.00005500
C	-1.20538300	-0.02976000	0.00013900
C	2.31201300	-1.47190800	-0.00027000
C	2.98014300	-0.23039100	-0.00015500
C	-1.33775200	1.33655100	0.00034400
H	0.41226300	-2.49041100	-0.00027400
H	2.79980900	1.91933000	0.00015000

H	0.12751100	2.88852400	0.00033300
H	4.06415900	-0.21082000	-0.00022700
H	-2.21580400	1.95952200	0.00051300
H	2.89387400	-2.38645800	-0.00042900
O	-2.15881600	-0.99844000	0.00014400
C	-3.50333800	-0.54424100	-0.00044600
H	-3.71584100	0.05370300	-0.89505400
H	-4.13102200	-1.43392400	-0.00073400
H	-3.71664100	0.05363000	0.89402200
Zero-point correction= 0.160987 (Hartree/Particle)			
Thermal correction to Energy= 0.170314			
Thermal correction to Enthalpy= 0.171259			
Thermal correction to Gibbs Free Energy= 0.126559			
Sum of electronic and zero-point Energies= -478.302716			
Sum of electronic and thermal Energies= -478.293388			
Sum of electronic and thermal Enthalpies= -478.292444			
Sum of electronic and thermal Free Energies= -478.337144			
Stable Neutral form (6-CH₃-indole)		6-CH₃-C₈H₆N	
0 1			
N	0.63341400	1.81366600	-0.00005700
C	0.17333600	-0.39067200	0.00001700
C	-0.40502500	0.90711400	-0.00004100
C	-0.67416500	-1.51034900	0.00004500
C	-1.78761800	1.10620700	-0.00007100
C	1.60613100	-0.22548900	0.00003500
C	-2.04823100	-1.31700100	0.00001400
C	-2.59911100	-0.02068300	-0.00004300
C	1.83614300	1.12463100	-0.00001100
H	-0.26139700	-2.51344300	0.00008900
H	-2.21543000	2.10297500	-0.00011600
H	0.53754500	2.81462500	-0.00009400
H	-3.67654800	0.09962700	-0.00006600
H	2.77320800	1.66053100	-0.00001400
H	-2.71209500	-2.17411400	0.00003500
C	2.63262700	-1.31705300	0.00009400
H	2.53581100	-1.96025700	0.88126300
H	2.53584200	-1.96032200	-0.88103100
H	3.64463600	-0.90552800	0.00009600
Zero-point correction= 0.156548 (Hartree/Particle)			
Thermal correction to Energy= 0.164674			

Thermal correction to Enthalpy= 0.165618			
Thermal correction to Gibbs Free Energy= 0.124035			
Sum of electronic and zero-point Energies= -403.085564			
Sum of electronic and thermal Energies= -403.077439			
Sum of electronic and thermal Enthalpies= -403.076495			
Sum of electronic and thermal Free Energies= -403.118077			
Stable Neutral form (6-N(CH₃)₂-indole)		6-N(CH₃)₂-C₈H₆N	
0 1			
N	-0.45285900	2.02922400	0.19444800
C	-0.40130300	-0.21004300	-0.07624900
C	-1.25244700	0.91378600	0.09686900
C	-0.98078000	-1.47717500	-0.25270500
C	-2.64474700	0.79439300	0.12269700
C	0.95740600	0.28513200	-0.06780800
C	-2.36249800	-1.59827100	-0.23055700
C	-3.18710800	-0.47272900	-0.03809800
C	0.87972400	1.64917600	0.09309700
H	-0.77972900	2.97875300	0.24193500
H	1.66182600	2.38894200	0.13558500
H	-3.28138500	1.66206000	0.25874400
H	-4.26397100	-0.59715800	-0.02279700
H	-2.81836800	-2.57186300	-0.37029300
H	-0.35928400	-2.34834300	-0.42349800
N	2.11340900	-0.50273300	-0.24531700
C	2.34728900	-1.49274700	0.80748000
H	1.43277700	-2.04470000	1.01897300
H	3.10943700	-2.20241400	0.47517900
H	2.68943600	-1.02706700	1.74766800
C	3.31975100	0.24011800	-0.57201900
H	4.11529600	-0.46357300	-0.82793400
H	3.13660400	0.88202100	-1.43618200
H	3.68178800	0.86806300	0.26245800
Zero-point correction= 0.201527 (Hartree/Particle)			
Thermal correction to Energy= 0.212127			
Thermal correction to Enthalpy= 0.213071			
Thermal correction to Gibbs Free Energy= 0.165852			
Sum of electronic and zero-point Energies= -497.710615			
Sum of electronic and thermal Energies= -497.700015			
Sum of electronic and thermal Enthalpies= -497.699071			
Sum of electronic and thermal Free Energies= -497.746289			