

## Computational Investigation of some Isomeric forms of 3-Ethyl Pyrrole

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**Abstract:** Computational studies based on 3-ethyl pyrrole and its isomeric forms using semi-empirical and Density Functional Theory (DFT- BLYP/6-31G\*) has been carried out. The addition of different substituents to the C-5 position of the 3-ethyl pyrrole ring led to significant changes in its properties. From the calculation, considering all the studied compounds, the parent compound was found to be less thermodynamically stable compared to the other four substituted compounds based on the lowest value of  $\Delta H$  which is  $-288.651\text{KJ/mol}$ . Compound D has the highest enthalpy change ( $\Delta H$ ) which is  $-681.949\text{KJ/mol}$ . The HOMO-LUMO energy gap ( $E_g$ ) were calculated using Density Functional Theory DFT B3LYP 6 -31G\*, and Moller Plesset MP|6-31G\*, to obtained compound with the lowest Energy gap. From the results, the energy gap of compounds were in the order;  $E < D < B < C < A$ . The polarizability of the compounds are in the order  $E > D > C > B > A$ . Therefore compound E is the most reactive based on its high polarizability and low  $E_g$  values.

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**Keywords:** HOMO, LUMO, Band gap, Density Functional theory, Semi-empirical, polarizability.

### 1.

#### Introduction

Pyrrole is a heterocyclic aromatic organic compound, which undergoes electrophilic aromatic substitution predominantly at the 2 and 5 positions and can undergo polymerization to yield several polypyrroles such as dipyrrole, tripyrrole, tetrapyrrole. Pyrrole undergoes electrophilic aromatic substitution predominantly at the 2 and 5 positions and also pyrrole can undergo polymerization to yield several polypyrroles such as dipyrrole, tripyrrole, tetrapyrrole etc. Tetrapyrroles are a class of chemical compounds containing four pyrrole rings held together by direct covalent bonds or by one-carbon bridges ( $=\text{CH}-$  or  $-\text{CH}_2-$  units), in either a linear or a cyclic fashion. Polypyrroles plays very crucial biochemical roles in living systems, such as hemoglobin and chlorophyll) and also are one of the major derivatives of organic conductors. (Mamardashvili, 1999)

Electrophilic substitution normally occurs at carbon atoms instead of at the nitrogen. Also it occurs preferentially at C-2 (the position next to the nitrogen atom) rather than at C-3 (if position 2- is occupied it occurs at position 3). This is due to fact that attack at C-2 gives more stable intermediate than the intermediate resulting from C-3 attack (it is stabilized by two resonance structure).

As expected for aromatic compound, pyrrole can react by electrophilic substitution In comparison to benzene, pyrrole is more reactive thus the substitution is easier and milder reagents can be used. The increased reactivity is a result of resonance which pushes the electrons from the N-atom into the ring making the c-atoms of pyrrole ring more electron rich

than in case of benzene. In fact pyrrole resembles most reactive benzene derivatives (phenols and amines). These substitutions take place by an initial electrophile addition, followed by a proton loss from the "onium" intermediate to regenerate the aromatic ring.

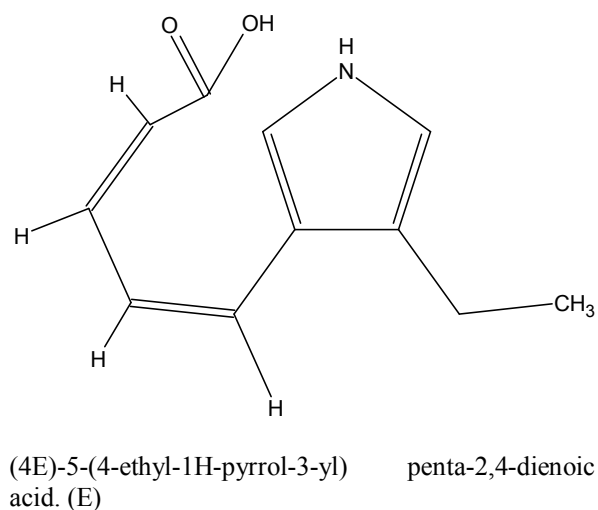
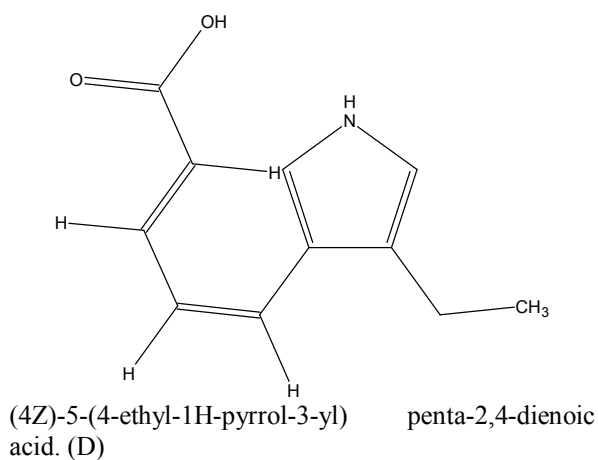
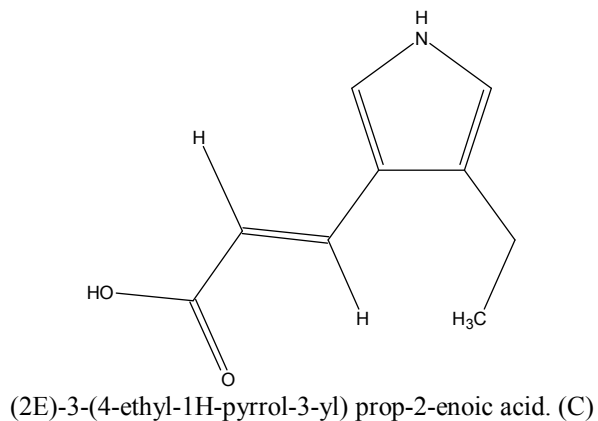
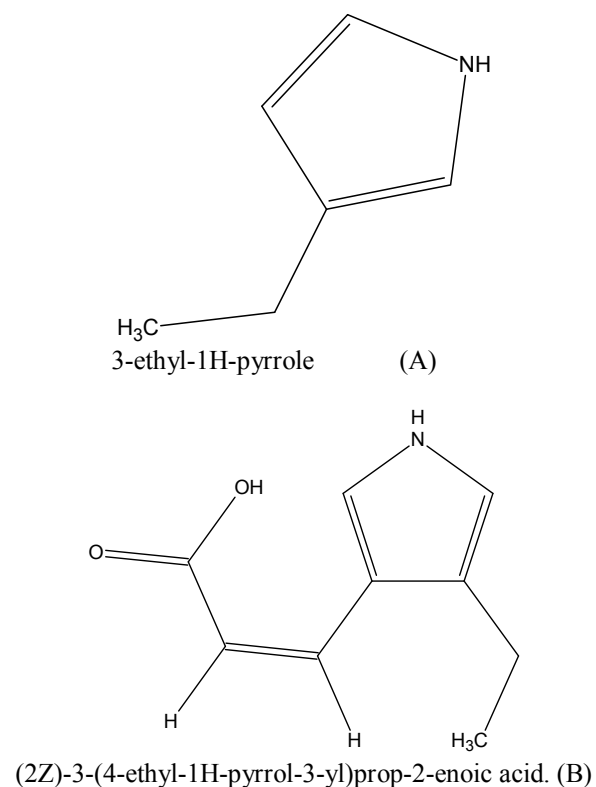
Functional substituents influence the substitution reactions of these heterocycles in the same fashion as they do for benzene. For example, when pyrrole has an electron withdrawing substituent e.g  $-\text{OH}$ ,  $\text{NO}_2$  at the C-2, it makes pyrrole less reactive, and electrophiles such as ethyl,  $\text{CH}_2\text{OC}-$ , will be directed to the C-4 i.e meta-directing substituent. While the presence of electron donating group such  $-\text{NH}_2$ , increases the reactivity and therefore become ortho and para-directing. The reactivity of pyrrole is also greatly influenced by steric effect which occurs especially when an electron withdrawing group is on the heteroatom (the nitrogen atom), this directs incoming electrophile to position 3.

Polypyrroles plays very crucial biochemical roles in living systems, such as hemoglobin and chlorophyll) and also are one of the major derivatives of organic conductors (Mamardashvili, 2000). It is among the most widely studied conjugated polymers that is environmentally stable and biocompatible. Its application is majorly due to its non-linear properties and it is mainly uses in photovoltaic cells. Pyrrole as an organic  $\pi$  conjugated material have been actively researched in the past decade because of their interesting potential applications in the film transistors, electroluminescent diodes, lasers, sensors and photovoltaic cells. Polypyrrole has also been

studied as potential candidate material for the fabrication of biosensors as well as for drug delivery devices.

Quantum chemical calculation using MP2 of pyrrole anions have been carried out. Steric hindrances destabilized N-adducts when a methyl substituent appears in a 2(5) position and the 2,5-dimethyl-1-pyrrolocarbodithioate anion turned out to be even less stable than the 2,5-dimethyl-3-pyrrolocarbodithioate anion. Pyrrole-1-carboxylates was calculated to be the most stable adducts of CO<sub>2</sub> with pyrrole anions. A density functional theory (DFT) based study on the interaction of poypyrrole and amino acids; leucine and glycine has been investigated (Dipojono *et al*, 2009). There are no reports on the studies on the Isomeric forms of 3-Ethyl Pyrrole, therefore this work is aimed at study using computational methods the structural properties of 3-Ethyl Pyrrole and its isomeric forms.

The structure of the 3-ethyl pyrrole and some of its isomeric forms such as (2Z)-3-(4-ethyl-1H-pyrrol-3-yl)prop-2-enoic acid, (2E)-3-(4-ethyl-1H-pyrrol-3-yl)prop-2-enoic acid, (4Z)-5-(4-ethyl-1H-pyrrol-3-yl)penta-2,4-dienoic acid and (4E)-5-(4-ethyl-1H-pyrrol-3-yl)penta-2,4-dienoic acid, are presented in Fig 1.

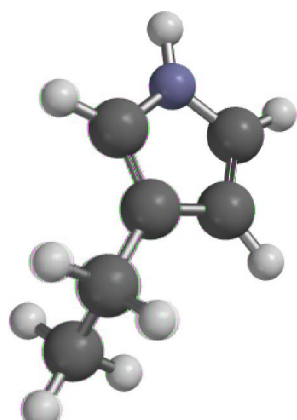


## 2 Computational Methodology

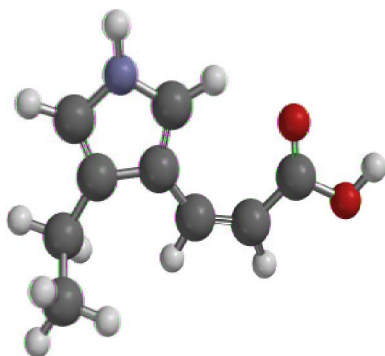
Semi-empirical AM1, PM3 and RM1 were used to calculate the heat of formation. Also Hartree Fock theory HF/6-31G\* and Density Functional Theory (DFT) B3LYP/6 -31G\*, Moller Plesset MP2/6-31G\* molecular orbital calculation were used in this study. The 3-ethyl pyrrole and the isomeric forms were studied and electronic properties such as HOMO,

LUMO, energy gap, geometric properties such as, bond angle, bond length, bond dihedral, thermodynamic properties such as enthalpy, entropy etc, infrared frequency vibration (IR) and ultra-violet/visible properties relatives to singlet species were fully optimized using their ground state; equilibrium geometries. All the calculations were performed using Spartan 14 software.

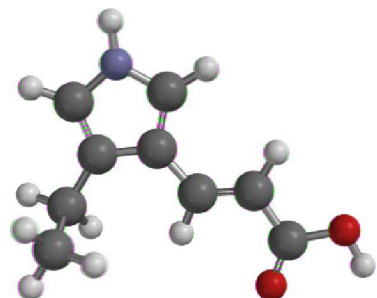
The optimized structures of studied systems are presented below in Fig 2



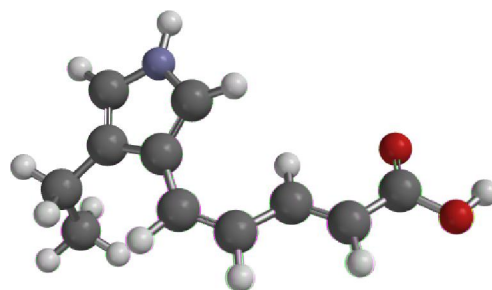
3-ethyl-1H-pyrrole (A)



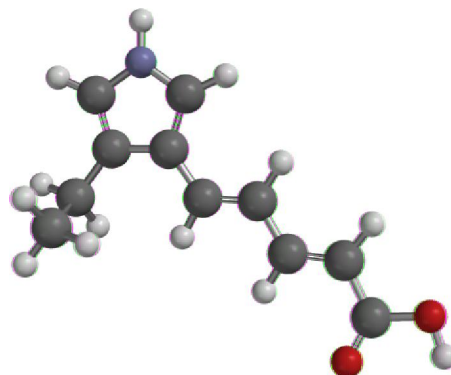
(B)(2Z)-3-(4-ethyl-1H-pyrrol-3-yl)prop-2-enoic acid



(C) (2E)-3-(4-ethyl-1H-pyrrol-3-yl) prop-2-enoic acid.



(4Z)-5-(4-ethyl-1H-pyrrol-3-yl) penta-2,4-dienoic acid. (D)



(4E)-5-(4-ethyl-1H-pyrrol-3-yl) penta-2,4-dienoic acid. (E)

### 3.0 Results And Discussion

#### 3.1 Geometry of optimized structures

Calculated theoretical bond lengths, bond angles and bond dihedral for the studied molecules are presented in Table 1 using DFT calculation with B3LYP and 6.31G\*. As shown in the tables above, N<sub>1</sub>-C<sub>1</sub>, N<sub>1</sub>-C<sub>4</sub>, C<sub>1</sub>=C<sub>2</sub>, C<sub>2</sub>-C<sub>3</sub>, C<sub>2</sub>-C<sub>3</sub>, for 3-ethyl pyrrole are 1.374, 1.377, 1.377, 1.431 and 1.381 respectively. For (2Z)-3-(4-ethyl-1H-pyrrol-3-yl) prop-2-enoic acid, 1.383, 1.358, 1.372, 1.452 and 1.396 respectively. For (2E)-3-(4-ethyl-1H-pyrrol-3-yl) prop-2-enoic acid, 1.381, 1.362, 1.375, 1.446 and 1.392 respectively. For (4Z)-5-(4-ethyl-1H-pyrrol-3-yl) penta-2,4-dienoic acid, 1.379, 1.364, 1.375, 1.447 and 1.393 respectively. For (4E)-5-(4-ethyl-1H-pyrrol-3-yl) penta-2,4-dienoic, 1.380, 1.363, 1.375, 1.446 and 1.393 respectively. All used methods give the minimal bond lengths for all the bonds which is in agreement with (Adejoro and Ibeji, 2013)

N<sub>1</sub>-C<sub>4</sub> and N<sub>1</sub>-C<sub>1</sub> which are between the pyrrole nitrogen and carbon atoms (see Fig.4.1) have different characteristics. In the 3-ethyl pyrrole which is the parent compound in this study, the value for the bond length for N<sub>1</sub>-C<sub>1</sub> is lower than the other four compounds as shown in Table 4.1 below. While the N<sub>1</sub>-C<sub>4</sub> bond length is higher than for the other four compounds. Also, the bond angles for H<sub>3</sub>-N<sub>1</sub>-C<sub>1</sub>, H<sub>3</sub>-N<sub>1</sub>-C<sub>4</sub>, N<sub>1</sub>-C<sub>1</sub>-C<sub>2</sub>, N<sub>1</sub>-C<sub>4</sub>-C<sub>3</sub>, and C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> decreases significantly but that of C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub> which is higher than

that of the reference compound. This is as a result of the ethyl which is attached to the C<sub>3</sub> position and

therefore the increase in the bond angles is due to the steric effect between the electrophile and the ring.

Table 1: Showing geometry bond length (Å), bond angle (°) and bond dihedral (°)

Bond length (Å)	A	B	C	D	E	Expt.
N <sub>1</sub> -C <sub>2</sub>	1.374	1.383	1.381	1.379	1.38	1.37
N <sub>1</sub> -C <sub>4</sub>	1.377	1.358	1.362	1.364	1.363	1.349
C <sub>1</sub> -C <sub>2</sub>	1.377	1.372	1.375	1.375	1.375	1.37
C <sub>2</sub> -C <sub>3</sub>	1.431	1.452	1.446	1.447	1.446	1.432
C <sub>3</sub> -C <sub>4</sub>	1.381	1.396	1.392	1.393	1.393	1.39
H <sub>3</sub> -N <sub>1</sub> -C <sub>1</sub>	125.26	125.1	125.1	125.24	125.12	
H <sub>3</sub> -N <sub>1</sub> -C <sub>4</sub>	125.18	124.48	124.91	124.78	124.91	
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	107.64	108.18	108.33	108.36	108.35	
N <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub>	108.37	107.86	108.02	108.09	108.06	
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	107.96	106.88	106.81	106.92	106.88	
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	106.47	106.66	106.85	106.68	106.88	
H <sub>3</sub> ,N <sub>1</sub> ,C <sub>1</sub> ,H <sub>1</sub>	-0.32	0.11	0.03	2.16	0.02	
H <sub>3</sub> ,N <sub>1</sub> ,C <sub>4</sub> ,C <sub>3</sub>	-179.41	-179.55	-179.04	178.08	-178.94	
C <sub>3</sub> ,C <sub>2</sub> ,C <sub>1</sub> ,N <sub>1</sub>	-0.10	-0.04	0.03	-0.58	0.05	
C <sub>2</sub> ,C <sub>3</sub> ,C <sub>4</sub> ,N <sub>1</sub>	0.03	0.03	0.12	-0.53	0.17	
C <sub>4</sub> ,C <sub>3</sub> ,C <sub>2</sub> ,C <sub>1</sub>	0.04	0.01	-0.10	0.68	-0.14	

Expt. Value (Nygaard, et al, 1969)

#### 4.2 Thermodynamic properties.

Table 4.2 Showing Thermodynamic Properties studied with DFT, HF, MP methods.

Thermodynamic properties	ZPE(Kj/mol)	ΔH°(au)	ΔG°(au)	ΔS°(J/mol°)	Cv(J/mol°)	
Compound A	DFT	365.90	-288.651	-288.688	396.66	107.24
	HF	391.51	-286.724	-286.761	327.47	98.29
	MP	370.62	-287.669	-287.706	329.51	107.40
Compound B	DFT	496.26	-554.576	-554.622	409.07	180.09
	HF	533.38	-551.173	-551.219	401.62	167.16
	MP	501.04	-552.850	-552.897	409.71	181.04
Compound C	DFT	494.63	-554.578	-554.625	412.65	182.07
	HF	531.39	-551.178	-551.224	405.15	169.27
	MP	499.64	-552.854	-552.900	413.15	182.62
Compound D	DFT	583.58	-681.945	-631.995	442.95	214.89
	HF	627.08	-628.025	-551.224	405.15	199.84
	MP	589.67	-629.957	-630.007	442.40	214.80
Compound E	DFT	582.79	-631.949	-631.999	447.08	216.01
	HF	625.89	-628.028	-628.078	438.28	201.29
	MP	588.51	-629.957	-630.009	447.11	216.54

The reaction energies, zero point energy, enthalpy and entropy calculated by DFT B3LYP/6-31G\*, MP MP2/6-31G\* and HF/6-31G\* are represented in Table 4.2 below. Since the lower ΔH is, the more thermodynamically stable it is. Owing to this fact, the parent compound is less thermodynamically stable compared to the other four substituted compounds. (2Z)-3-(4-ethyl-1H-pyrrol-3-yl)prop-2-enoic acid and (2E)-3-(4-ethyl-1H-pyrrol-3-

yl)prop-2-enoic acid are quite stable with the values -554.576, -551.173, -552.850 and -554.578, -551.178, -552.854 respectively for the DFT, HF, MP methods respectively. But the (4Z)-5-(4-ethyl-1H-pyrrol-3-yl) penta-2,4-dienoic acid and (4E)-5-(4-ethyl-1H-pyrrol-3-yl) penta-2,4-dienoic with values -681.945, -628.025, -629.957 and -631.949, -628.028, -629.957 respectively for the DFT, HF and MP methods respectively. The slight difference between the

compound B and compound C is due to the geometric isomerism and this is also true for the slight difference between the enthalpy change of compounds D and E. Therefore, Cis isomers are usually more stable thermodynamically than the Trans isomers.

The spontaneity of the reaction is dependent on the value of  $\Delta G$ . The negative values of  $\Delta G$  indicate that the reaction is spontaneous shows that it is an endothermic reaction. According to the results, all reactions are going to be spontaneous but the higher the substituents that are added increases the value of  $\Delta G$  and then the reaction readily occurs.

Table 4.3 Showing heat of formation in kJ/Mol using semi empirical calculation.

Compound	AM1	RM1	PM3
A	108.891	39.048	54.564
B	-217.326	-280.169	-255.914
C	-224.808	-293.245	-273.368
D	-161.679	-228.862	-208.421
E	-168.679	-231.671	-213.195

### 4.3 Electronic properties.

Energy gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), or simply HOMO-LUMO gap (HLG;  $\Delta E_g$ ), also called band gaps, is a key parameter which determines the molecular admittance because it is a measure of the electron density hardness. In order to determine the compound with the least Energy gap, the following methods are used. Ab initio HF/6-31G\*, DFT BLYP/6-31G\* and MP2/6-31G\* methods as shown in the table 4.4 below. Comparing the values obtained before and after substitution, it was noticed that each substituents reduced the band gap. The effect was more with isomers with higher Molecular Mass. This is due to the increase in the electron pulling or accepting ability of the different substituents. The order of energy gap of compounds is  $E < D < B < C < A$  which implies that the compound E is the most reactive because of the lower energy gap is which makes it easy for electrons to move between HOMO and LUMO.

Electronic properties	Compound A			Compound B			Compound C			Compound D			Compound E		
	DFT	HF	MP	DFT	HF	MP	DFT	HF	MP	DFT	HF	MP	DFT	HF	MP
HOMO	-5.38	-7.85	-7.70	-5.61	-7.84	-7.78	-5.70	-8.01	-7.96	-5.47	-7.79	-7.66	-5.39	-7.64	-7.56
LUMO	1.43	5.67	5.46	-1.19	2.80	2.54	-1.19	2.80	2.57	-1.62	2.35	2.07	-1.59	2.30	2.00
Energy gap	6.81	13.52	13.16	4.42	10.64	10.32	4.51	10.81	10.53	3.85	10.14	9.73	3.80	9.94	9.56

Table 4.4 Showing the Electronic properties in eV of the studied compounds using DFT, HF and MP methods of calculation.

### 4.4 Quantitative Structure Activity Relationship (QSAR)

QSAR	Polarizability( $\text{\AA}^3$ )	Area( $\text{\AA}^2$ )
Compound A	DFT	49.52
	HF	47.67
	MP	47.82
Compound B	DFT	54.72
	HF	53.14
	MP	53.32
Compound C	DFT	54.76
	HF	53.15
	MP	53.33
Compound D	DFT	57.52
	HF	55.90
	MP	56.10
Compound E	DFT	57.57
	HF	55.98
	MP	52.20

The reactivity of a compound is highly dependent on its polarizability. Considering the DFT

B3LYP/6-31G\* result, the compounds D and E which are (4Z)-5-(4-ethyl-1H-pyrrol-3-yl)penta-2,4-dienoic acid and (4E)-5-(4-ethyl-1H-pyrrol-3-yl)penta-2,4-dienoic acid respectively have the highest polarizability values which are  $57.52(\text{\AA}^3)$  and  $57.57(\text{\AA}^3)$  respectively. The addition of these substituents therefore increases the reactivity of the ring.

Table 4.5 showing the Quantitative Structure Activity Relationship of the studied compounds using DFT, HF, MP Methods.

### Chapter Five Conclusion

Computational studies of 3-ethyl pyrrole and some of its derivatives using semi-empirical, DFT, Møller Plesset and Hartree-fork have been carried out. Addition of some substituents into the backbone of 3-ethyl pyrrole led to changes in the structural properties and physical properties of the compound.

From the calculation, considering all the studied compounds studied, the parent compound was found to be less thermodynamically stable compared to the other four substituted compounds with respect to the value of  $\Delta H$ . (2Z)-3-(4-ethyl-1H-pyrrol-3-yl)prop-2-

enoic acid and (2E)-3-(4-ethyl-1H-pyrrol-3-yl)prop-2-enoic acid are quite stable with the values -554.576, -551.173, -552.850 and -554.578, -551.178, -552.854 respectively for the DFT, HF, MP methods respectively. But the (4Z)-5-(4-ethyl-1H-pyrrol-3-yl)penta-2,4-dienoic acid and (4E)-5-(4-ethyl-1H-pyrrol-3-yl)penta-2,4-dienoic with values -681.945, -628.025, -629.957 and -631.949, -628.028, -629.957 respectively for the DFT, HF and MP methods respectively.

Conclusively, the slight differences between the compound B and compound C is due to the geometric isomerism, this is also true for the slight difference in the physical properties of compounds D and E. Hence, the cis isomers are usually more stable thermodynamically than the Trans isomers. Since the spontaneity of the reaction is dependent on the value of  $\Delta G$ , the reactions involving the trans isomer are usually more spontaneous than those involving the cis isomers. Also bond lengths are smaller for Cis isomers than for trans isomers. Also the electronic properties of the studied compounds were carried out and in order to get the compound with the lowest energy gap, the parameters from the results of DFT BLYP/6-31G\* were considered showing that the energy gap of compounds  $E < D < B < C < A$  which implies that the compound E is the most reactive because of the lower energy gap is which makes it easy for electrons to move between HOMO and LUMO. The polarizability of the compounds are in the order  $E > D > C > B > A$ . Therefore compound E is the most reactive since the high polarizability values dictates the extent of its reactivity.

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