

# A density functional theory study on the porphyrin isomers: effect of meso-bridge length, relative stabilities, *cis-trans* isomerism

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Dedicated to Dr. A. V. Rama Rao on his 70<sup>th</sup> birthday

(received 06 Dec 04; accepted 18 Feb 05; published on the web 03 Mar 05)

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## Abstract

B3LYP/6-311+G\*\* calculations are employed to study the structures, stabilities of 1,2 (*syn*) and the 1,3 (*anti*) tautomeric forms of porphyrin isomers with varying meso-bridge lengths. A total of 46 structures obtained by considering the geometrical isomers of 1,2 (*syn*) and the 1,3 (*anti*) tautomeric forms, 44 were characterized as distinct minima on potential energy surface. Among the *anti* and *syn* tautomeric form the porphycene isomer 4a and 4a' is computed to be the most stable with a strong intramolecular hydrogen bonding. A  $-(CH)_2-$  linker in Z form with significant  $\pi$ -delocalization and the E form isomers are somewhat distorted into bowl-like structure in order to avoid the steric repulsion between the inner protons. In the isomers with trimethine interpyrrole linker, the E forms 7b and 7b' are having lower energy than the Z form due to the unstrained bond angles in these isomers and the Z form is destabilized by severe bond angle. In isomer [4.0.0.0], which has connectivity with the maximum possible bipyrrrolic, linkage Z isomer is having high energy this is due to possibly strained bonds that are directly connected to the pyrrole rings.

**Keywords:** Porphyrin isomers, density functional theory, tautomerism, meso-bridges, minima

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## Introduction

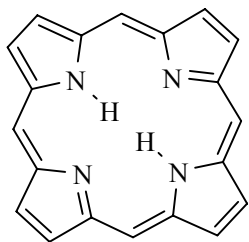
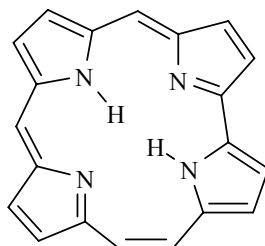
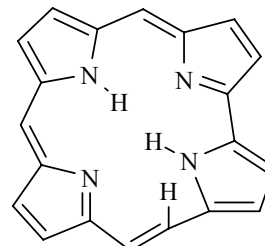
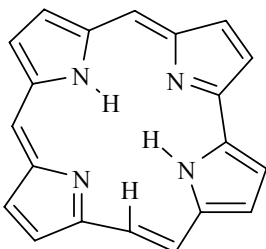
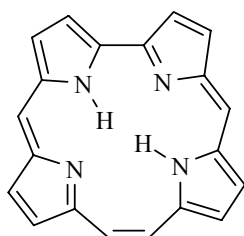
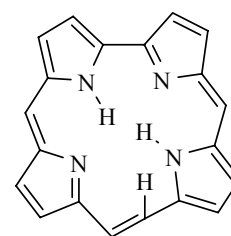
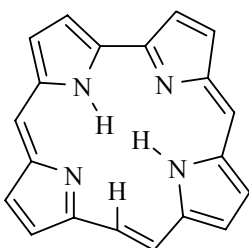
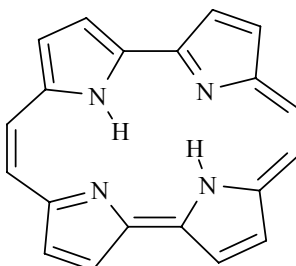
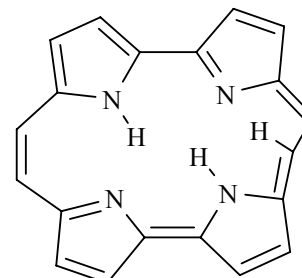
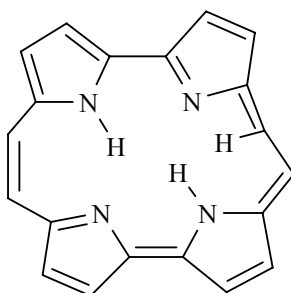
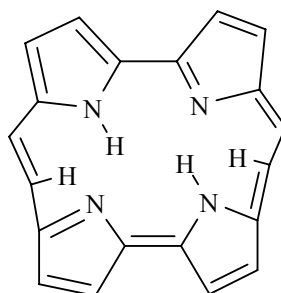
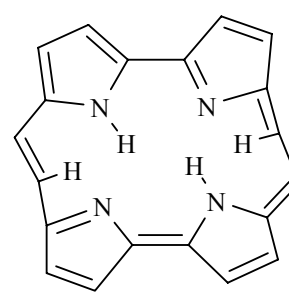
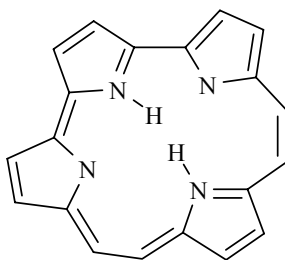
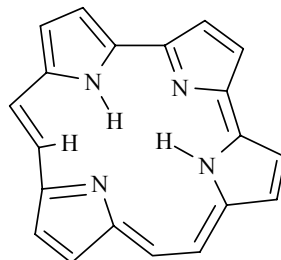
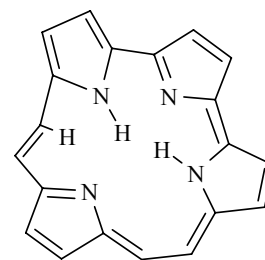
The study of porphyrins and related compounds has been developed into a subject of interdisciplinary interest due to their importance and relevance spanning a range of fields such as chemistry, biology and medicine.<sup>1,2,3</sup> Porphyrins with their extended  $\pi$ -electron networks and exhibit high stability and have displayed applications in advanced materials as components in organic metals and in photodynamic therapy in the treatment of cancer and dermatological

diseases.<sup>3</sup> The biological significance and the potential technological applications of porphyrins and related isomers are traced to their unique structural features.<sup>4,5,6</sup>

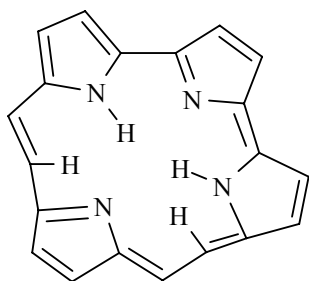
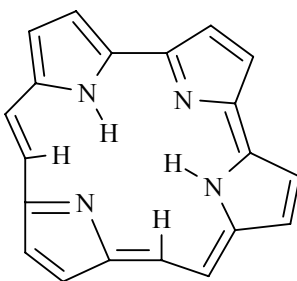
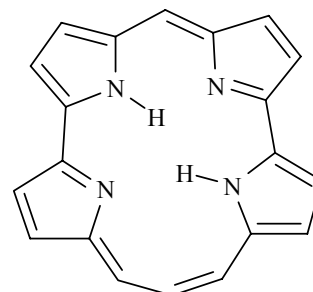
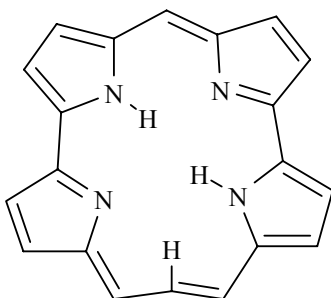
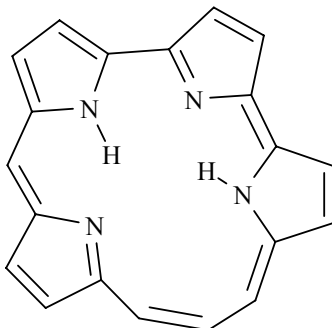
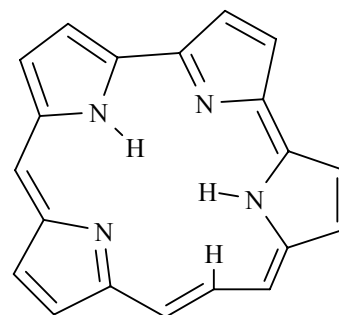
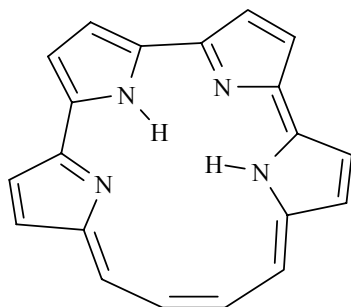
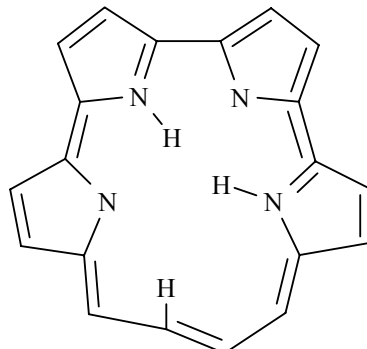
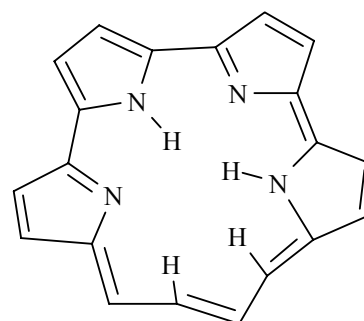
Recent successes in the syntheses of porphyrin isomers have opened up a new direction in porphyrin chemistry. The research groups of Vogel, Sessler, Furuta and others have synthesized a wide variety of porphyrin analogues.<sup>7,8,9</sup> Many of the porphyrins are of interest as novel ligands for transition metals, and some have potential practical applications.<sup>3</sup> Porphycenes, the first porphyrin isomers to be synthesized show promise as drugs in photodynamic cancer therapy.<sup>10</sup> Structural variants such as ring or bridge extended, reshuffled,<sup>11,12</sup> inverted<sup>13</sup>, N- and C-fused<sup>14</sup>, contracted and core-modified porphyrins<sup>15</sup> have been synthesized and they continue to exhibit novel physico-chemical properties. Synthetically this endeavor is challenging which is compounded by the fact that these structural variations may lead to configurational isomers. Their relatively large molecular sizes, symmetry, rich light absorption and emission properties have triggered meaningful interplay between theory and experiment.<sup>16, 17,18,19</sup> It has been observed that the properties of porphyrin isomers such as, hemiporphycene [2.1.1.0], porphycene [2.0.2.0], isoporphycene [3.0.1.0],<sup>7,12,16</sup> corphycene [2.1.0.1],<sup>8</sup> are akin to those of porphyrin especially in their ability to form a wide range of stable complexes.<sup>20,21,22,23,24</sup>

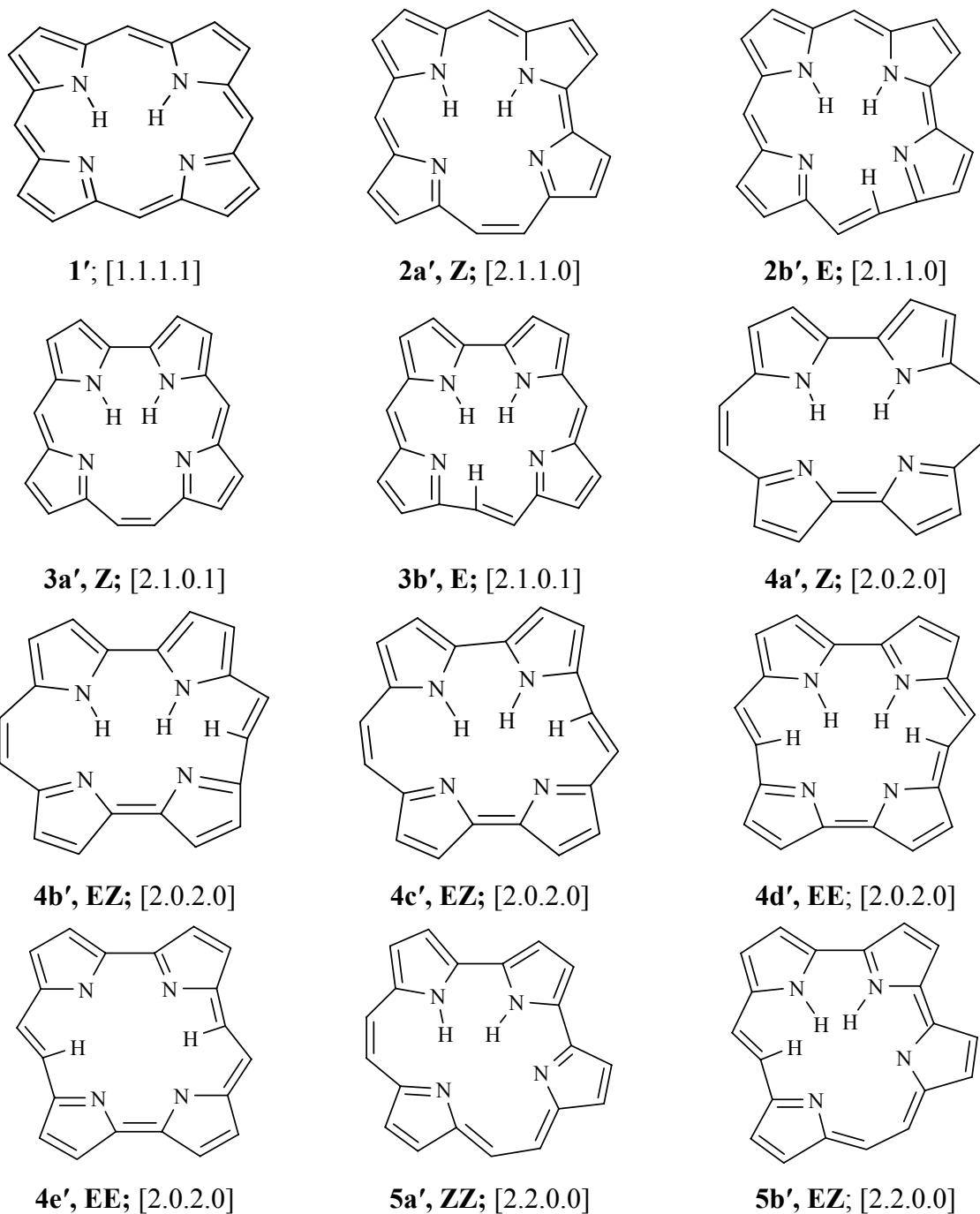
Wu et al. carried out density functional calculations using both the BLYP/3-21G and BLYP/6-31G\*\* methods on free-base porphyrin and its possible isomers with an N<sub>4</sub> – metal coordination core.<sup>20</sup> Ghosh et al. examined whether tetrapyrrolic isomers can accommodate trans double bonds.<sup>18</sup> while these studies addressed some important issues on the stability ordering of the porphyrin isomers, the structural and stabilities of various other possible porphyrin isomers were not considered. Considering the importance of the understanding the relative stability of the porphyrin isomers, we would like to explore the causative reasons such as angle strain, internal hydrogen bonding, inner proton repulsion, meso bridge length, cis-trans isomerism etc.<sup>20,21,25</sup>

In this present study we concentrated particularly on tetrapyrrolic isomers of porphyrin isomers with N<sub>4</sub> cores. Two types of tautomers (a) *anti* (the imino protons on the I and III ring, Scheme 1); (b) *syn* (imino protons at II and I ring, Scheme 2) were taken into consideration. In this study, eight classes, depending on the nature of bridging, were considered, viz. freebase porphyrin [1.1.1.1], hemiporphycene [2.1.1.0], corphycene [2.1.0.1], porphycene [2.0.2.0], isoporphycene [3.0.1.0], [2.2.0.0], [3.1.0.0] and [4.0.0.0]. Schemes 1 and 2 depicts the structures considered along with the general nomenclature used in the study for these isomers. Except for the freebase **1**, all other classes involve geometrical isomerism Z (cis) and E (trans), so overall 46 porphyrin isomers of *syn* and *anti* tautomeric forms were studied.

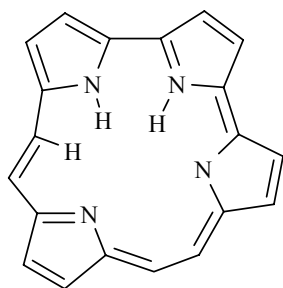
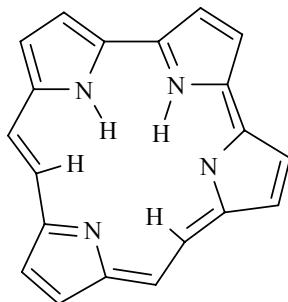
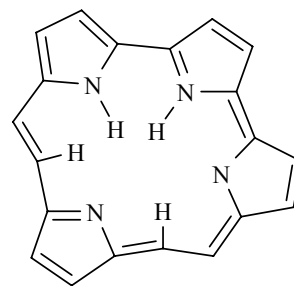
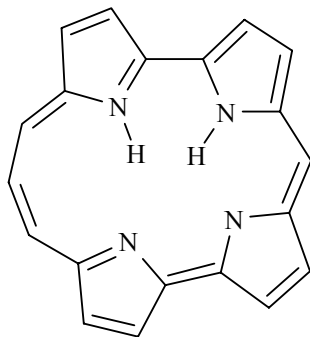
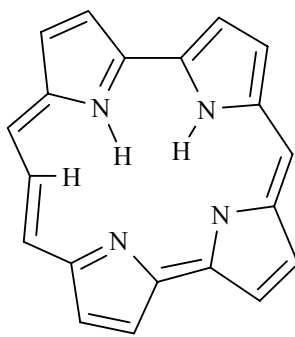
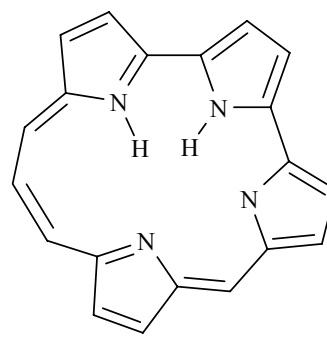
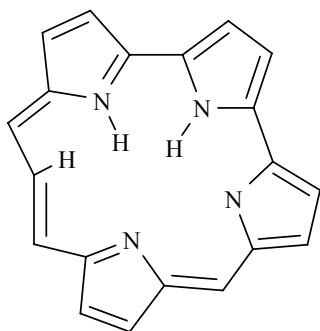
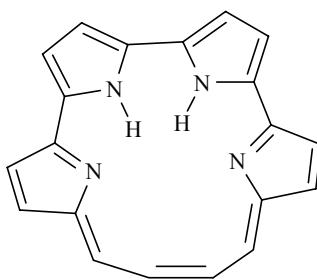
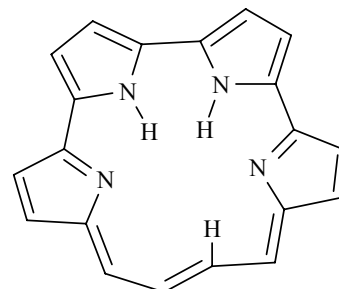
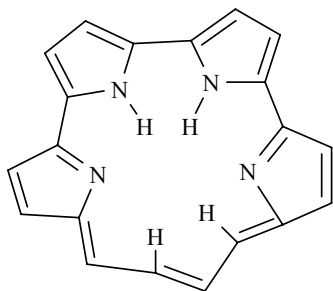
**1**; [1.1.1.1]**2a, Z**; [2.1.1.0]**2b, E**; [2.1.1.0]**2c, E**; [2.1.1.0]**3a, Z**; [2.1.0.1]**3b, E**; [2.1.0.1]**3c, E**; [2.1.0.1]**4a, Z**; [2.0.2.0]**4b, ZE**; [2.0.2.0]**4c, ZE**; [2.0.2.0]**4d, EE**; [2.0.2.0]**4e, EE**; [2.0.2.0]**5a, Z**; [2.2.0.0]**5b, ZE**; [2.2.0.0]**5c, ZE**; [2.2.0.0]

Scheme 1

**5d, EE; [2.2.0.0]****5e, EE; [2.2.0.0]****6a, Z; [3.0.1.0]****6b, E; [3.0.1.0]****7a, Z; [3.1.0.0]****7b, E; [3.1.0.0]****8a, Z; [4.0.0.0]****8b, ZE; [4.0.0.0]****8c, EE; [4.0.0.0]****Scheme 1. (Continued).**



Scheme 2

**5c', EZ;** [2.2.0.0]**5d', EE;** [2.2.0.0]**5e', EE;** [2.2.0.0]**6a', Z;** [3.0.1.0]**6b', E;** [3.0.1.0]**7a', E;** [3.1.0.0]**7b', Z;** [3.1.0.0]**8a', E;** [4.0.0.0]**8b', EZ;** [4.0.0.0]**8c', EE;** [4.0.0.0]

Scheme 2. Continued

### Computational details

B3LYP/6-31G calculations on all the structures considered in the study were optimized with planar geometries and the resultant stationary points were subjected to frequency calculations. Frequency calculations reveal that most of the planar structures do not correspond to minima. In such cases, following the normal modes of the imaginary frequencies, the minimum energy structures were obtained which display significant out-of-plane distortions. Many of these non-planar minimum energy structures are highly puckered and in some cases the pyrrolic rings got inverted. This shows that the structures have very high strain in the planar geometries, so we intended to calculate the energy difference between the planar structure and the puckered non-planar structures and reported as distortion energies. The cavity size also large for the puckered structures. The EE isomers are more puckered compared to the EZ isomers. All the minima are characterized by frequencies calculations, which shows all real frequencies. Single point calculations were done using 6-311+G\*\* basis set on B3LYP/6-31G optimized geometries. 6-311+G\*\* basis set is a triple  $\zeta$  basis set with polarization function on the heavy atoms and hydrogens as well as diffuse functions on the heavy atoms. The choice of using a B3LYP/6-31G geometries is entirely due to the economic reasons. As the previous studies<sup>6,18-20</sup> indicate that a better quality basis set is required to get better estimates, single point calculations were done at higher level of theory. All the calculations were performed using Gaussian 98 suite of programs.<sup>26</sup>

### Results and Discussion

The different types of isomers are possible by varying methine bridges in addition to the parent porphyrin moiety. Considering all the possible geometric isomers, a total of 46 structures of 1,3 (*anti*) and 1,2 (*syn*) tautomers were considered in the present study, are given in Schemes 1 and 2. The relative energies were calculated from the energy difference between porphyrin isomer **1** in *anti* isomers and porphyrin isomer **1'** in *syn* isomers.

#### *Anti* and *syn* tautomeric forms

The relative energies, enthalpies, Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies, distortion energies of *anti* tautomers of porphyrin isomers obtained at B3LYP level using the 6-31G and 6-311+G\*\* basis sets are given in Table 1. The B3LYP/6-31G optimized geometries of *anti* tautomeric structures and the relative energies with enthalpy correction are given in Figure 1. The variation in relative energies of *anti* (1,3) and *syn* (1,2) tautomeric porphyrin isomers obtained at B3LYP/6-31G and 6-311+G\*\* levels of theory are given in Figure 3. Considering all the possible cis-trans isomers of 1,3 (*anti*) and 1,2 (*syn*) tautomers totally 46 porphyrin isomers are resulted. Among 46 isomers **8c** collapsed to the EZ isomer **8a** and Z isomer **6a'** collapsed to the *anti* tautomeric structure **6a** due to closely presented imido protons. Thus, the total number of isomers reduced to 44. Porphyrin isomer **4a** is the most stable isomeric form. The porphyrin isomer **4a** is -0.4 kcal/mol more stable than the porphyrin isomer **1**.

**Table 1.** Relative energies ( $\Delta E$ , in kcal/mol), Enthalpies ( $\Delta H$ , in kcal/mol), HOMO ( $E_{\text{HOMO}}$ , in eV) and LUMO ( $E_{\text{LUMO}}$ , in eV) energies and the number of imaginary frequencies (NIMG) of *anti* tautomer of porphyrin isomers obtained at B3LYP level using the 6-31G and 6-311+G\*\* basis sets

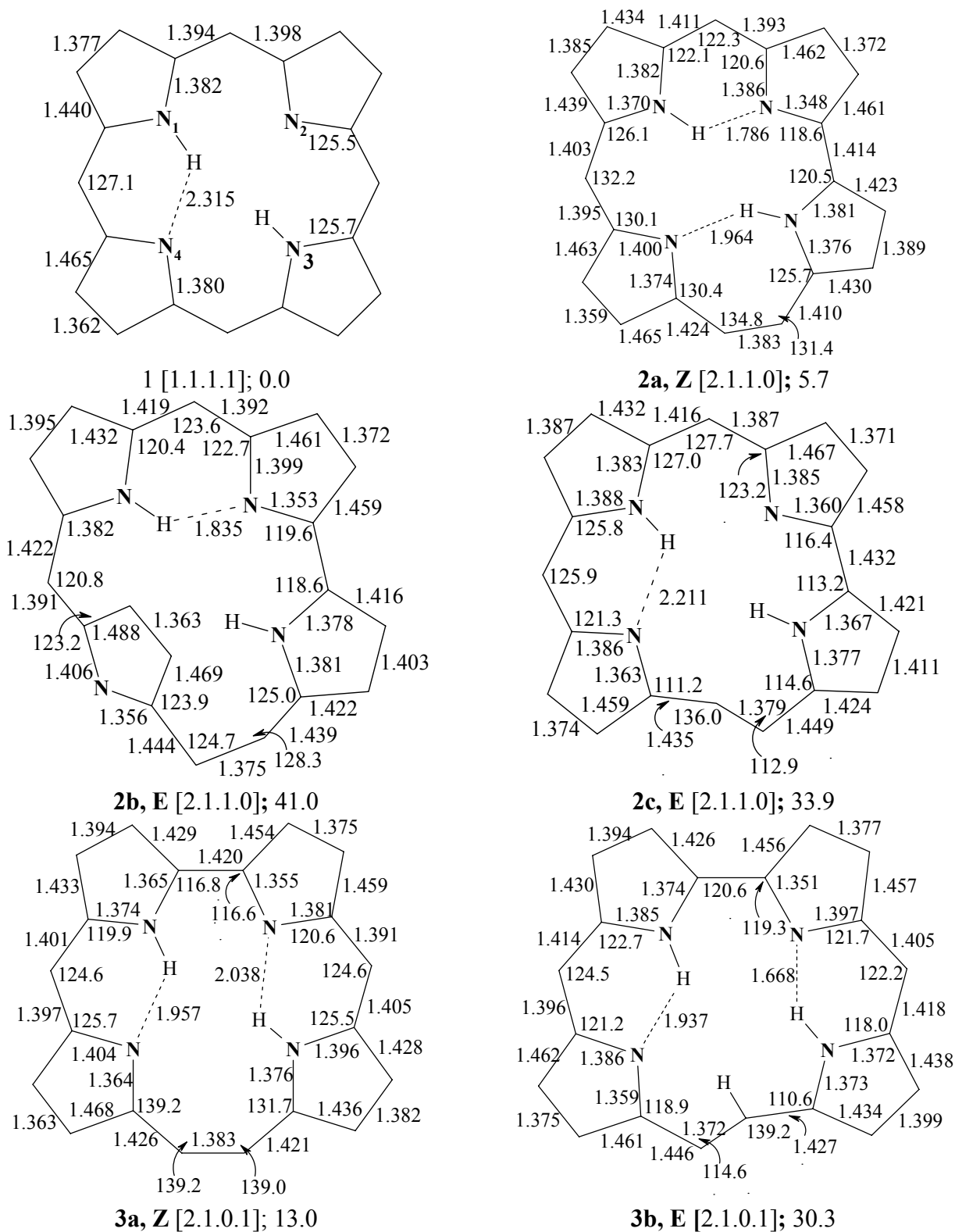
Struct.	B3LYP/6-31G						B3LYP/6-311+G** <sup>a</sup>		
	$\Delta E$	NIMG	$\Delta E^b$	$\Delta H$	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$	$\Delta E^b$	$\Delta E^c$
<b>1a</b>	0.0	0	0.0	0.0	-5.16	-2.30	0.0	0.0	0.0
<b>2a</b>	4.4	0	0.0	0.0	-5.30	-2.60	5.7	0.0	5.7
<b>2b</b>	42.7	1	15.5	-0.1	-5.23	-2.77	41.1	15.6	41.0
<b>2c</b>	36.2	2	15.2	-0.7	-5.34	-2.77	34.6	15.7	33.9
<b>3a</b>	12.2	0	0.0	0.2	-5.35	-2.39	12.8	0.0	13.0
<b>3b</b>	29.9	1	1.9	-0.6	-5.32	-2.49	30.9	2.6	30.3
<b>3c</b>	29.7	1	2.1	-0.5	-5.33	-2.51	30.2	3.4	29.7
<b>4a</b>	-3.0	0	0.0	-0.7	-5.34	-2.88	0.3	0.0	-0.4
<b>4b</b>	56.3	1	14.0	-0.5	-5.12	-2.99	53.7	15.0	53.2
<b>4c</b>	47.2	2	28.2	-1.2	-5.30	-3.18	45.1	27.7	43.9
<b>4d</b>	82.6	3	30.2	-1.0	-5.09	-2.92	76.8	33.2	75.8
<b>4e</b>	82.9	2	26.7	-1.0	-5.09	-2.92	76.7	30.0	75.7
<b>5a</b>	33.5	1	0.1	0.3	-5.31	-2.96	32.7	0.4	33.0
<b>5b</b>	50.1	2	7.7	-0.4	-5.24	-3.06	48.8	8.8	48.4
<b>5c</b>	62.1	1	16.9	-0.6	-5.20	-2.95	57.7	19.3	57.1
<b>5d</b>	83.1	3	25.5	-0.9	-5.12	-2.96	77.0	29.1	76.1
<b>5e</b>	86.4	3	32.5	-1.2	-5.19	-3.11	79.2	35.7	78.0
<b>6a</b>	19.2	0	0.0	-0.1	-5.36	-2.48	21.2	0.0	21.1
<b>6b</b>	27.5	1	1.0	0.1	-5.26	-2.54	27.9	1.2	28.0
<b>7a</b>	42.2	0	0.0	0.2	-5.30	-2.78	41.4	0.0	41.6
<b>7b</b>	33.2	2	0.5	-0.2	-5.23	-2.79	33.0	1.1	32.8
<b>8a</b>	75.4	1	1.6	-1.2	-4.89	-2.64	70.6	4.2	69.4
<b>8b</b>	42.2	1	0.1	-0.3	-5.23	-3.04	41.0	1.6	40.7

<sup>a</sup> Single point calculations were done on B3LYP/6-31G optimized geometries.

<sup>b</sup> The energy computed by taking the difference between the planar structure and the corresponding minimum energy structure. All these values are in kcal/mol.

<sup>c</sup> The relative energies with enthalpy correction at B3LYP/6-311+G\*\* level.





**Figure 1.** The B3LYP/6-31G optimized geometries (bond lengths in Å and bond angles in degrees) of *anti* porphyrin isomers. The relative energies obtained at B3LYP/6-311+G\*\* with enthalpy correction are given in kcal/mol.

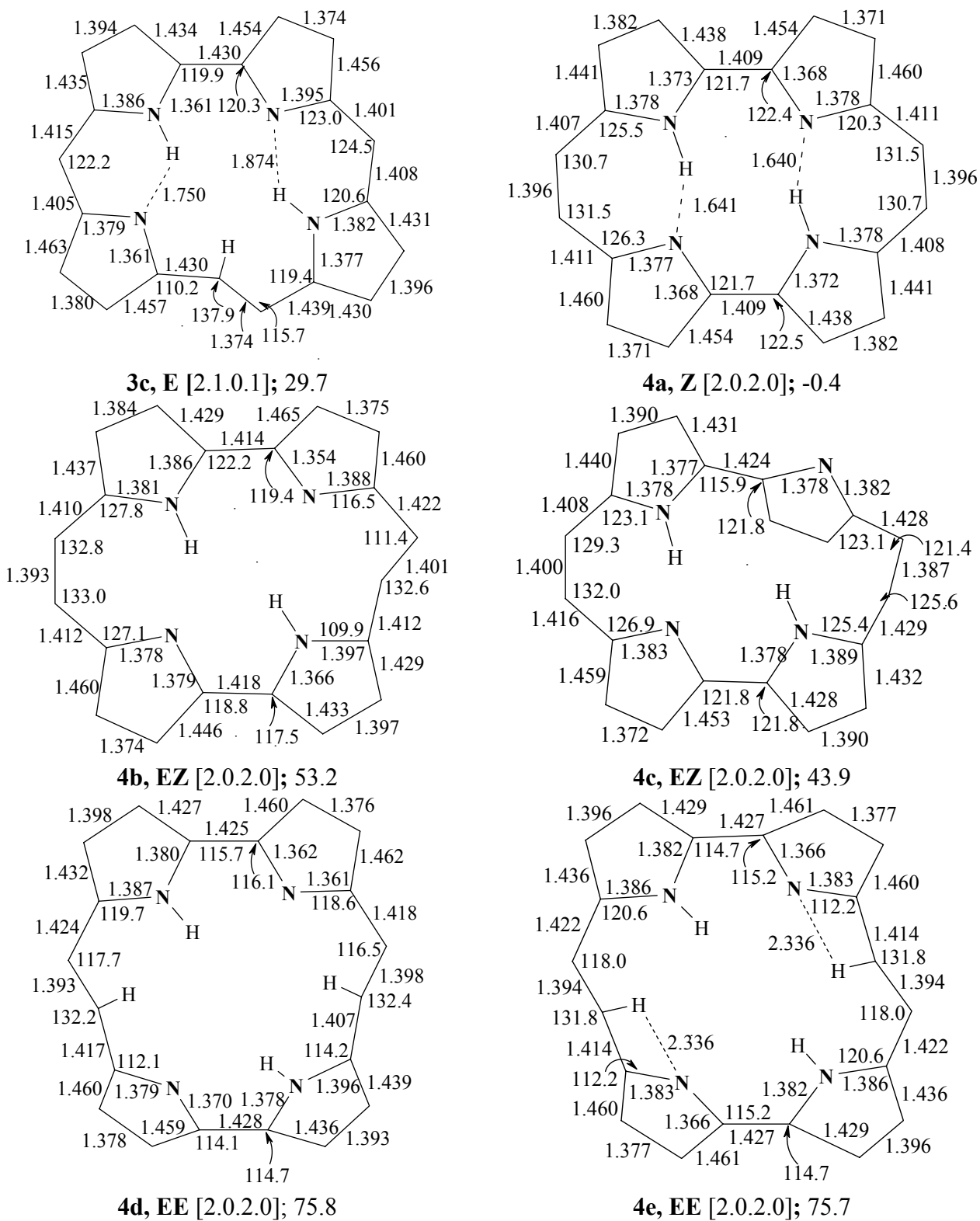


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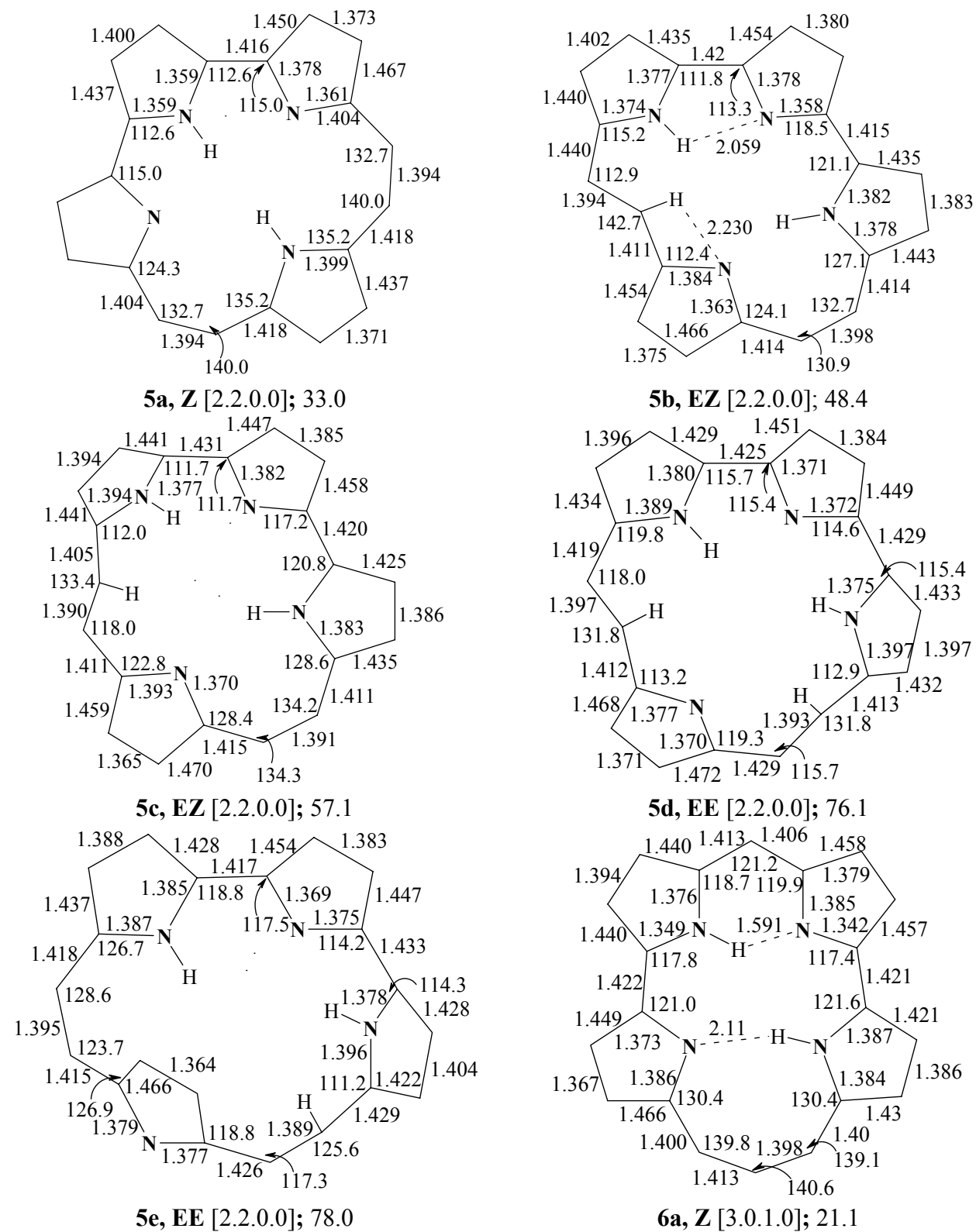
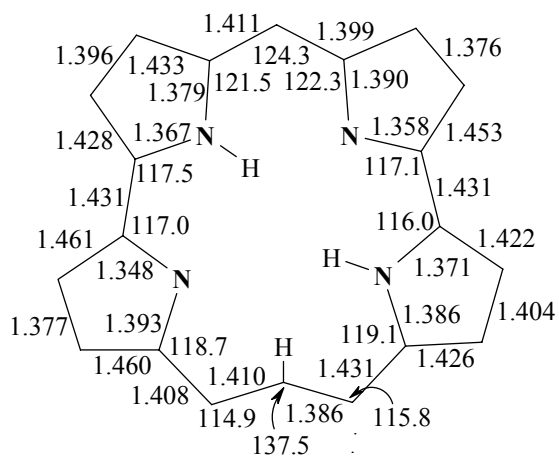
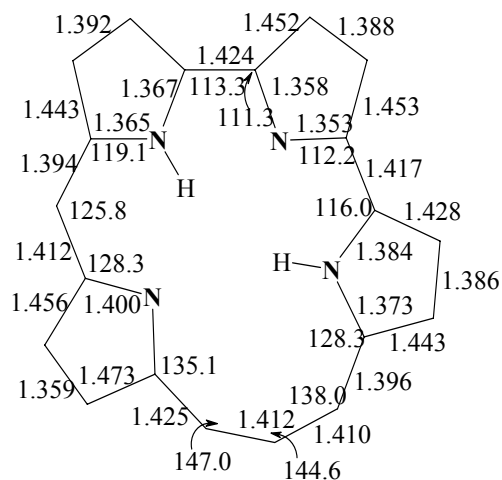
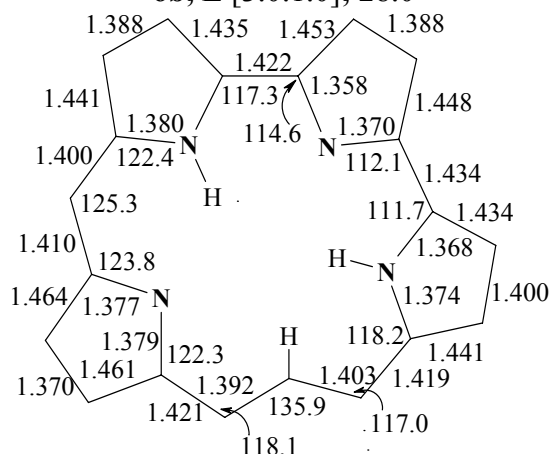
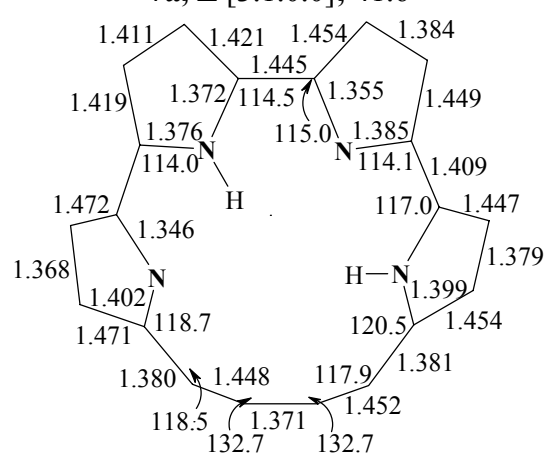
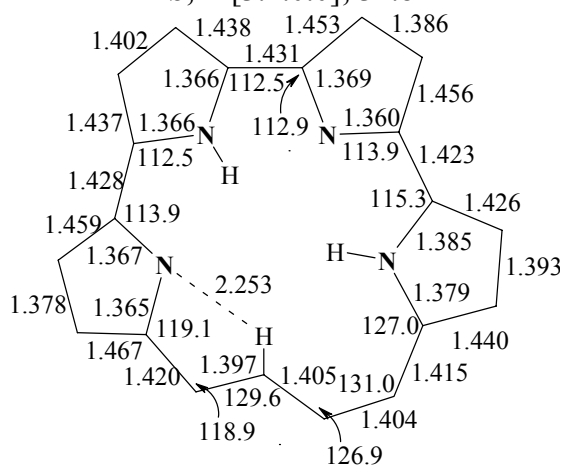
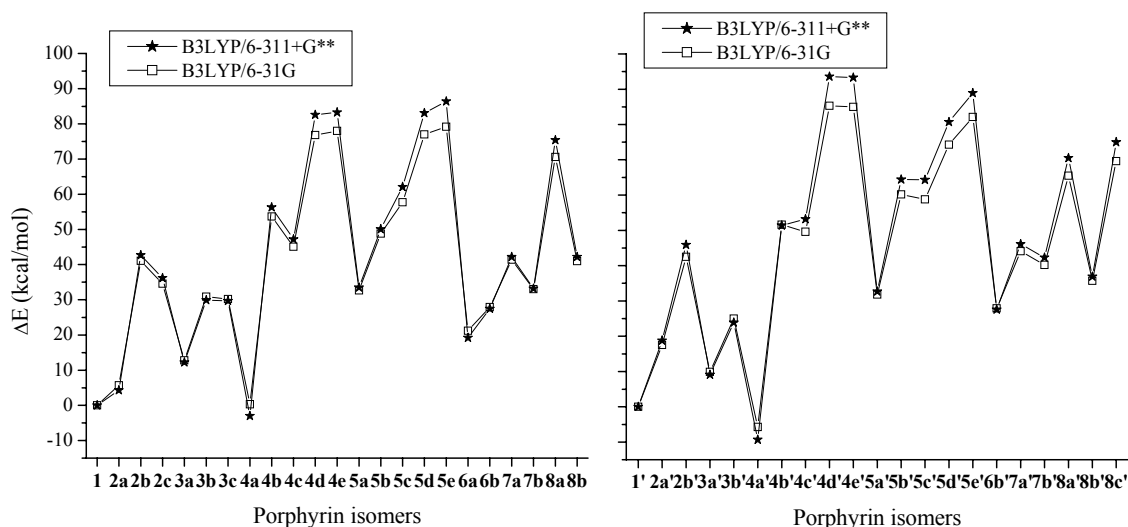


Figure 1. Continued

**6b, E** [3.0.1.0]; 28.0**7a, Z** [3.1.0.0]; 41.6**7b, E** [3.1.0.0]; 32.8**8a, Z** [4.0.0.0]; 69.4**8b, EZ** [4.0.0.0]; 40.7**Figure 1. Continued**

Isomers **5a**, **6a**, **7a** and **8a** are much less stable than porphyrin isomer **4a** and **1**. In hemiporphycenes [2.1.1.0], the Z isomer **2a** is more stable than the E isomers **2b** and **2c**. Isomer **2c** is more stable than **2b** by 7 kcal/mol and the isomer **2b** undergoes ring inversion due to a highly repulsive interaction between tautomeric carbons and inner proton repulsion. In corphycenes [2.1.0.1], the Z isomer **3a** is more stable than the E isomers **3b** and **3c**. Isomers **3b** and **3c** are having energy difference around 0.6 kcal/mol. In porphycenes [2.0.2.0], three different isomeric forms are possible: Z form (**4a**), EZ form (**4b** and **4c**) and EE form (**4d** and **4e**). Among porphycene isomers, **4a** is most stable due to strong hydrogen bonding. In EZ form and EE forms, the EZ form isomers **4b** and **4c** more stable than the EE form isomers **4d** and **4e** by 20-30 kcal/mol. The destabilizations of these isomers are traced due to the inner proton repulsion between the imino proton and proton present in the methine bridge. In isomer [2.2.0.0], like porphycene isomers, three different types of isomers are possible for these isomers. In EZ form and EE forms, the EZ form isomers **5b** and **5c** more stable than the EE form isomers **5d** and **5e** this is due to the presence of inner CH group. In isomers [3.0.1.0], the Z isomer is strongly favored energetically over the E isomer. The E forms **7b** and **7b'** are having lower energy than the Z form due to the unstrained bond angles in these isomers. In isomers [4.0.0.0] which has connectivity with the maximum possible bipyrrolic linkages and all the methine bridging groups are placed together, the EZ isomer **8b** is having lower energy than the Z form **8a**. Attempts to locate the **8c** was futile, the structure is collapsing with the isomer **8a**.

The relative energies, enthalpies, HOMO and LUMO energies, distortion energies of *syn* tautomers of porphyrin isomers obtained at B3LYP level using the 6-31G and 6-311+G\*\* basis sets are given in Table 2. The B3LYP/6-31G optimized geometries of *anti* tautomeric structures and the relative energies with enthalpy correction are given in Figure 2. The variation in relative energies of *anti* (1,3) and *syn* (1,2) tautomeric porphyrin isomers obtained at B3LYP/6-31G and 6-311+G\*\* levels of theory are given in Figure 2.



**Figure 2.** Relative energies of *anti* tautomers (a) and *syn* tautomers (b) of porphyrin isomers obtained at B3LYP/6-31G and 6-311+G\*\* levels of theory.

In the *syn* tautomeric structures of porphyrin isomer, **4a'** is the most stable isomeric form and is about 6 kcal/mol more stable than porphyrin due to its exceptional strong hydrogen bonding. Isomers **5a'**, **7a'** and **8a'** are much less stable than porphyrin isomer **1'**. Similarly like *anti* porphyrin isomers, hemiporphycenes [2.1.1.0] and corphycenes [2.1.0.1], the Z isomer **2a** and **3a** are more stable than the E isomers **2b** and **3b** this is due to the inner proton repulsion.

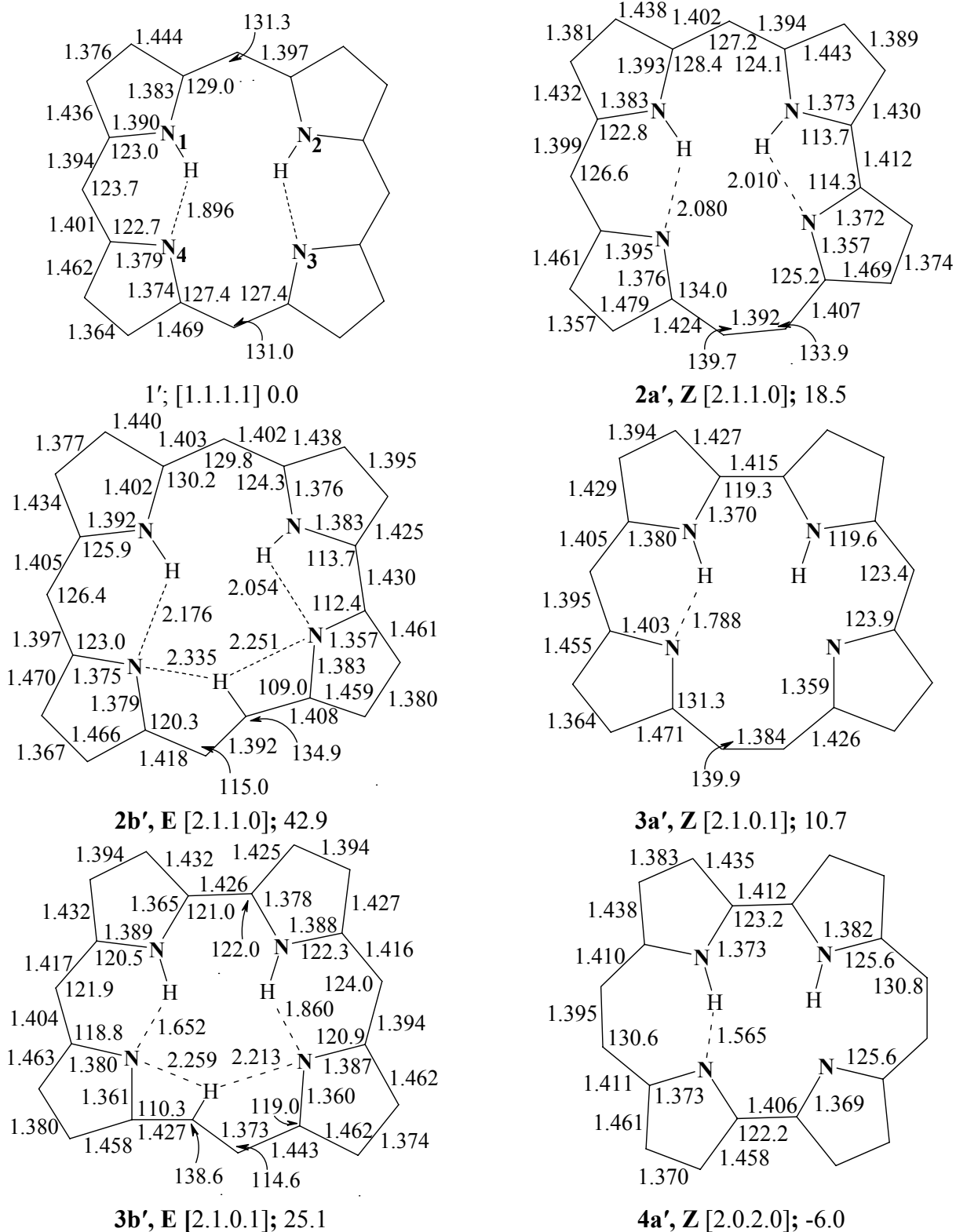
**Table 2.** Relative energies ( $\Delta E$ , in kcal/mol), Enthalpies ( $\Delta H$ , in kcal/mol), HOMO ( $E_{\text{HOMO}}$ , in eV) and LUMO ( $E_{\text{LUMO}}$ , in eV) energies and the number of imaginary frequencies (NIMAG) of *syn* tautomer of porphyrin isomers obtained at B3LYP level using the 6-31G and 6-311+G\*\* basis sets

Struct.	B3LYP/6-31G					B3LYP/6-311+G** <sup>a</sup>			
	$\Delta E$	NIMAG	$\Delta E^b$	$\Delta H$	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$	$\Delta E^b$	$\Delta E^c$
<b>1a'</b>	0.0	0	0.0	0.0	-5.19	-2.34	0.0	0.0	0.0
<b>2a'</b>	18.8	0	0.0	1.0	-5.24	-2.67	17.5	0.0	18.5
<b>2b'</b>	45.9	1	10.4	0.4	-5.11	-2.75	42.5	12.3	42.9
<b>3a'</b>	9.1	0	0.0	0.8	-5.36	-2.43	9.9	0.0	10.7
<b>3b'</b>	23.9	1	3.5	0.1	-5.31	-2.46	25.0	2.5	25.1
<b>4a'</b>	-9.3	0	0.0	-0.3	-5.33	-2.87	-5.7	0.0	-6.0
<b>4b'</b>	51.4	2	24.6	0.1	-5.20	-3.09	49.6	26.4	49.7
<b>4c'</b>	53.2	1	18.0	0.1	-5.25	-3.03	51.6	18.6	51.7
<b>4d'</b>	93.6	4	45.2	0.3	-5.14	-2.95	85.0	44.7	85.3
<b>4e'</b>	93.3	3	34.3	-0.3	-5.19	-2.95	85.3	31.9	85.0
<b>5a'</b>	32.7	0	0.0	1.2	-5.33	-2.98	31.8	0.0	33.0
<b>5b'</b>	64.4	3	13.4	0.7	-5.26	-3.09	60.2	13.3	60.9
<b>5c'</b>	64.3	3	25.6	0.5	-5.18	-2.99	58.8	24.6	59.3
<b>5d'</b>	80.7	3	32.9	0.3	-5.14	-2.95	74.3	29.9	74.6
<b>5e'</b>	88.9	3	29.7	0.0	-4.87	-2.95	82.1	27.1	82.1
<b>6b'</b>	27.6	3	2.5	0.4	-5.21	-2.53	27.9	2.2	28.3
<b>7a'</b>	46.1	1	0.5	1.0	-5.31	-2.82	44.1	0.1	45.1
<b>7b'</b>	42.3	1	3.2	0.9	-5.25	-2.84	40.2	2.9	41.1
<b>8a'</b>	70.5	2	10.4	0.1	-4.94	-2.53	65.5	9.2	65.6
<b>8b'</b>	36.9	2	3.4	1.0	-5.29	-3.04	35.7	2.3	36.7
<b>8c'</b>	75.0	1	29.2	0.2	-5.22	-3.09	69.6	26.2	69.8

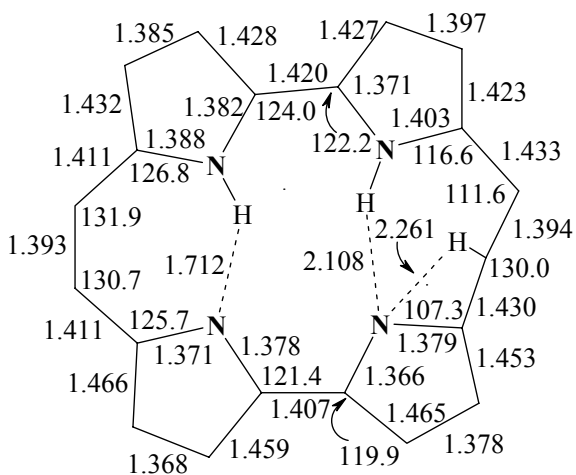
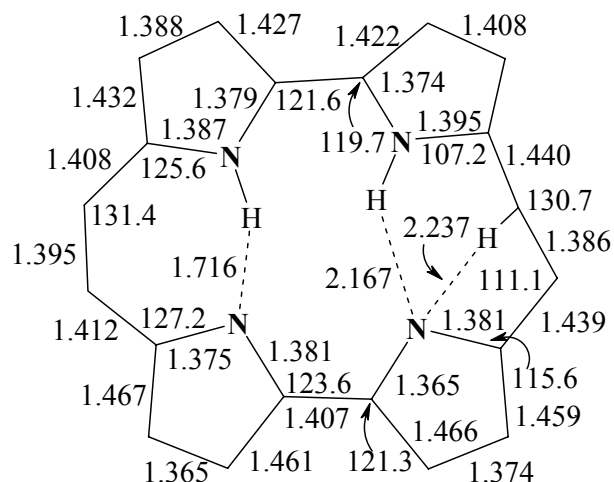
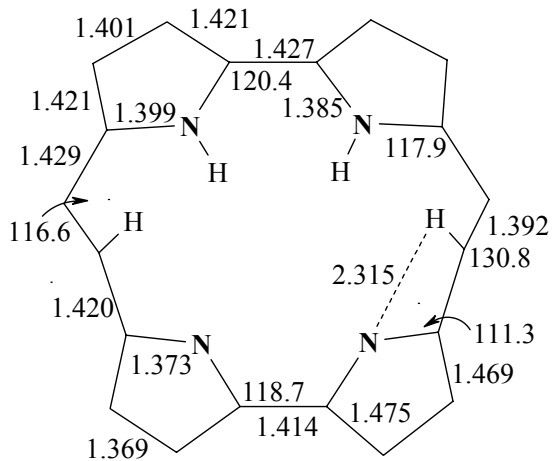
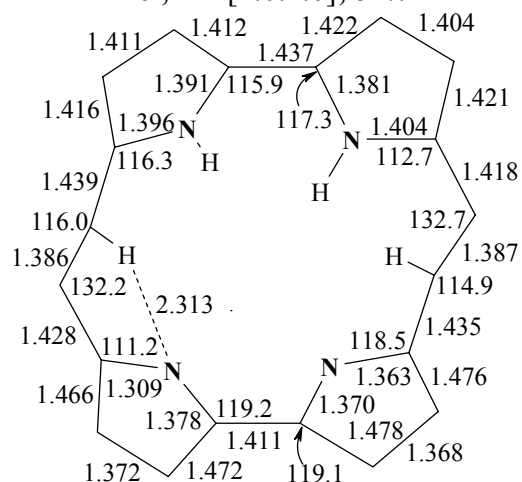
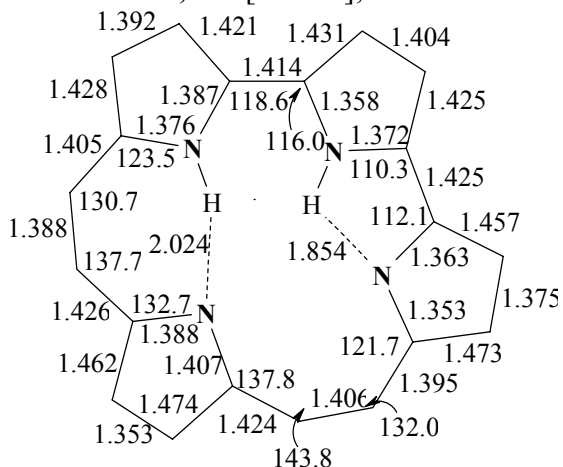
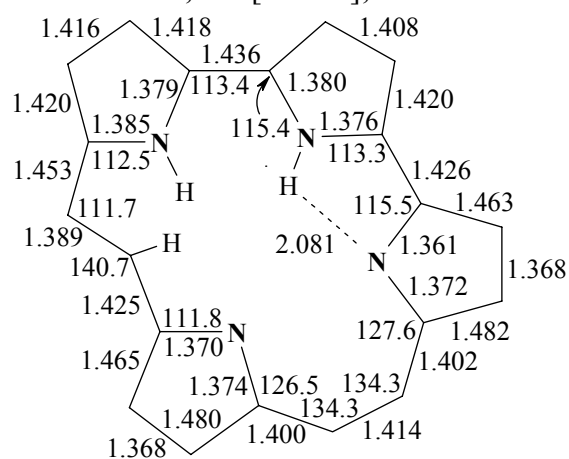
<sup>a</sup> Single point calculations were done on B3LYP/6-31G optimized geometries.

<sup>b</sup> The energy computed by taking the difference between the planar structure and the corresponding minimum energy structure. All these values are in kcal/mol.

<sup>c</sup> The relative energies with enthalpy correction at B3LYP/6-311+G\*\* level.



**Figure 3.** The B3LYP/6-31G optimized geometries (bond lengths in Å and bond angles in degrees) of *syn* porphyrin isomers. The relative energies obtained at B3LYP/6-311+G\*\* with enthalpy correction are given in kcal/mol.

**4b'**, EZ [2.0.2.0]; 49.7**4c'**, EZ [2.0.2.0]; 51.7**4d'**, EE [2.0.2.0]; 85.3**4e'**, EE [2.0.2.0]; 85.0**5a'**, Z [2.2.0.0]; 33.0**5b'**, EZ [2.2.0.0]; 60.9**Figure 3.** Continued



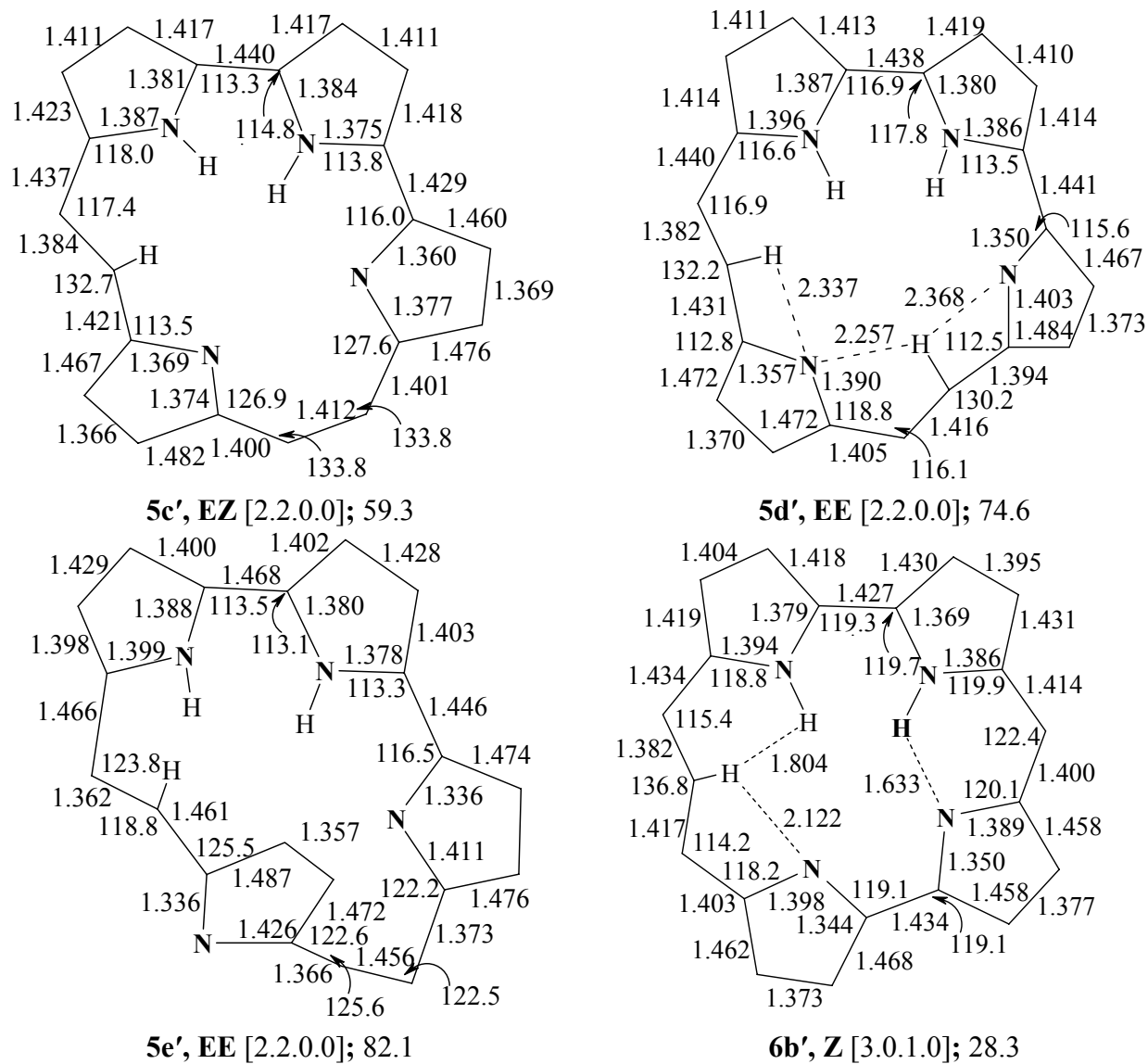
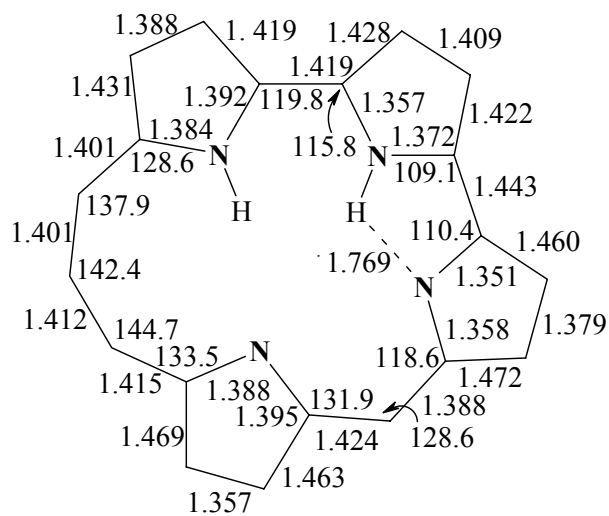
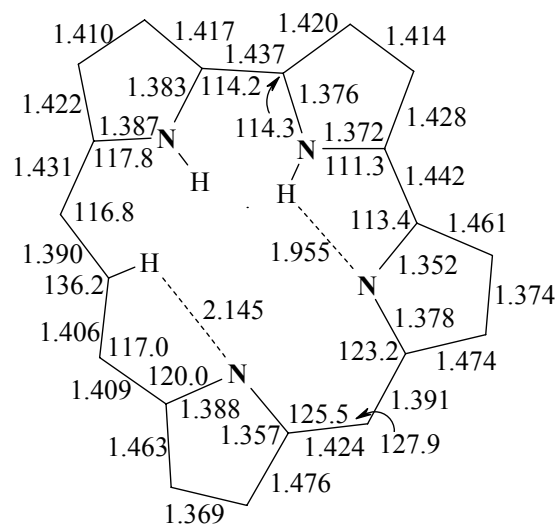
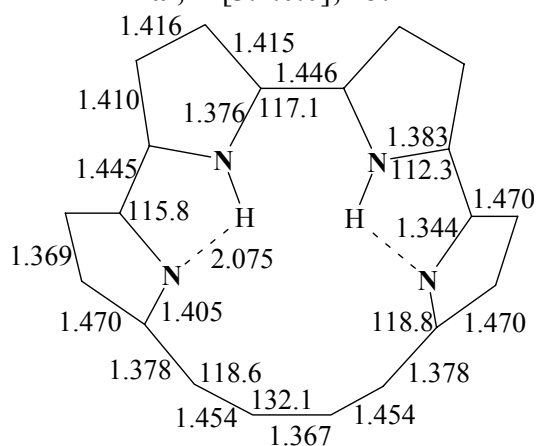
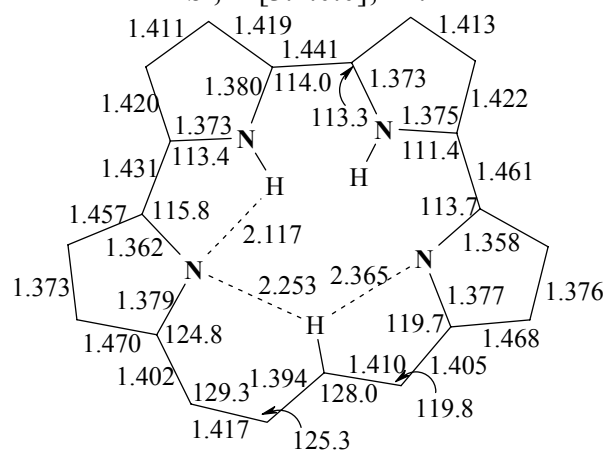
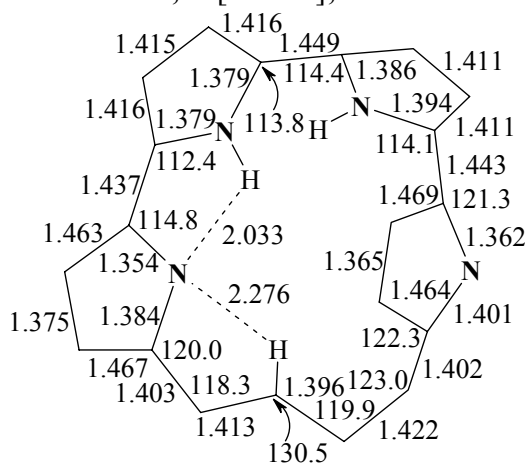


Figure 3. Continued

**7a', Z** [3.1.0.0]; 45.1**7b', E** [3.1.0.0]; 41.1**8a', Z** [4.0.0.0]; 65.6**8b', EZ** [4.0.0.0]; 36.7**8c', EE** [4.0.0.0]; 69.8**Figure 3. Continued**

In porphycenes [2.0.2.0] and [2.2.0.0], like *anti* porphyrin isomers there are three different isomeric forms. Isomer **4a'** is most stable than all other porphycene isomers. This is due to strong hydrogen bonding. In EZ form and EE forms, the EZ form isomers **4b'** and **4c'** more stable than the EE form isomers **4d'** and **4e'**. The Z isomer **5a** is more stable than the EZ isomers **5b** and **5c** and EE isomer **5d** and **5e**. In EZ form and EE forms, the EZ form isomers **5b** and **5c** more stable than the EE form isomers **5d** and **5e** this is due to the presence of inner CH group.

In isomers [3.0.1.0], attempts to locate the planar form of **6a'** was futile, the structure is collapsing with the *anti* tautomeric isomer **6a**. In [3.1.0.0], the E form is more stable than the Z forms. The E form **7b'** are having lower energy than the Z form due to less steric strain in these isomers. In isomers [4.0.0.0], which have connectivity with the maximum possible bipyrrolic linkages the EZ, isomer **8b** is having lower energy than the Z and EE form **8a** and **8c** due to less angle strain. Comparison of Table 1 and 2 indicates that the trends in the relative energy ordering of the 1,3 (*anti*) and 1,2 (*syn*) tautomeric forms are very similar.

### Geometrical isomerism

Except for the porphyrin isomers **1** and **1'** geometrical isomerism is possible for all the isomeric forms considered for the *syn* and *anti* isomers. The relative stabilities of the geometrical isomers have attracted the theoreticians and experimentalist. The E and Z form especially affects the metal-binding properties of ligand. The important bond lengths and bond angles for all the *anti* and *syn* porphyrin isomers obtained at B3LYP/6-31G optimization are given in Figure 3.

In hemiporphyrin [2.1.1.0] and corroporphycene [2.1.0.1], three isomers are considered in *anti* tautomeric forms (one Z form and two E forms). In *syn* tautomeric forms one Z form and one E form is considered. In porphycene [2.0.2.0] and [2.2.0.0] five isomers one Z form, two EZ form and two EE form in both *syn* and *anti* tautomeric forms. The isomers [2.1.1.0], [2.1.0.1], [2.0.2.0], [2.2.0.0] having two  $-(CH)-$  linkages, prefer Z isomers **2a**, **2a'**, **3a**, **3a'**, **4a**, **4a'**, **5a** and **5a'** this preference was due to the less steric interactions involving the inner CH group comparing to its E, EE and EZ isomers.

In isomers isoporphycene [3.0.1.0] and [3.1.0.0], one E form and one Z form was considered in both *syn* and *anti* tautomers. In isomers [4.0.0.0], which have connectivity with the maximum possible bipyrrolic linkages one Z form, one EZ form and one EE form was considered. In [3.1.0.0] the E forms are more stable than Z forms. The E forms **7b**, **7b'** are more stable than the Z forms **7a** and **7a'** due to the less angle strain in these isomers. Isomers [4.0.0.0] **8a** and **8a'** are computed to be least stable compare to all other Z isomers and EZ isomer **8b** and **8b'** favored than Z isomers (**8a** and **8a'**) and EE isomers (**8c'**), this may be due to less angle strain in the EZ form. In isomers porphycenes [2.0.2.0], [2.2.0.0] the EZ isomers are more stable than the EE isomers in both the *anti* and *syn* tautomeric forms.

### Effect of meso-bridge length on the relative stabilities

The relative energy differences seem to critically depend on the length and position of the meso bridges. In hemiporphycenes [2.1.1.0], corroporphycenes [2.1.0.1], porphycenes [2.0.2.0],

[2.2.0.0] having two  $-(CH)-$  linkages, prefer Z isomers **2a**, **2a'**, **3a**, **3a'**, **4a**, **4a'**, **5a** and **5a'** this preference was due to the less steric interactions involving the inner CH group comparing to its E, EE and EZ isomers.

When a  $-(CH)_2-$  linker is in the Z form, isomers are nearly planar with significant  $\pi$ -delocalization. In contrast, the corresponding E isomers have distorted structures with bowl-like geometries, which are traced due to steric repulsive interactions involving the inner protons. But, [3.1.0.0] the E forms are more stable than the Z forms, indicating higher angle strain in the latter. In isomers [4.0.0.0], which have connectivity with the maximum possible bipyrrolic linkages, Z isomer is computed to be relatively unstable. The variation in number of methine groups drastically alters the stability in these class of compounds.

### Angle strain

Next to the hydrogen-bonding interactions, the strained bond angles dictate the relative stability ordering of the porphyrin isomers. All skeletal bond angle for the *anti* and *syn* structures are given in Figure 1 and Figure 3 respectively. The lower stability of isomers **5a**, **5a'**, **6a**, **7a**, **7a'**, **8a** and **8a'** in both *syn* and *anti* forms may directly traced to the severe angle strain in these isomers. The isomers of types [2.2.0.0], isoporphycenes [3.0.1.0], [3.1.0.0], [4.0.0.0] are destabilized due to the absence of bridging methine groups, which results in the angle strain for the tetrapyrroles and possibly due to the strained bonds that are directly connect to pyrrole rings. Bond angle strain is perhaps the most important factor contributing to the high energies in Z form in all [3.0.1.0], [4.0.0.0] isomers. The E isomers **7b** and **7b'** are having lower energy than the Z form, due to the unstrained bond angles in these isomers and the Z form is destabilized by severe bond angle strain in the trimethine interpyrrole linker. Isomers **8a** and **8c'** are computed to be the least stable among the [4.0.0.0.] isomers. The EZ isomers (**8b** and **8b'**) appear to be much less strained and importantly one of the hydrogens of the methine chain involve in hydrogen bond with the nitrogens.

### Distortion energies

The  $\pi$ -delocalization and planarity has been treated as important factors to impart stability to porphyrins. However, as the planar form of a large number of isomers are not minima on the potential energy hypersurface, the puckering is often related to the strain in the planar form. We termed the energy difference between the planar structure and the corresponding minimum energy structure as the distortion energy. The distortion energies, which quantifies the amount strain in the planar geometry of the isomers, of the *anti* and *syn* porphyrin isomers are given in Table 1 and Table 2. In *anti* porphyrin isomers all the Z form isomers except **5a** and **8a** are planar. All other isomers have positive distortion energies, indicating that the nonplanar structures are more stable. In *syn* porphyrin isomers all the Z form isomers except **7a'** and **8a'** are planar. Isomers having positive distortion energies, signifying that nonplanar structures are more stable. The distortion energies are more for the EE form isomers than EZ forms. This is due to the inner proton repulsions in case of EE isomers.

### Hydrogen bonding

Porphyrin isomers show some strong hydrogen bonds in most of the structures due to the close proximity of the four nitrogen atoms. In *anti* porphyrin isomer **1**, the N---H--N distance is 2.315 Å and in *syn* porphyrin isomer **1'** the distance is 1.896 Å (Figure 1 and 3). In *anti* and *syn* porphycene isomers **4a** and **4a'** features strong hydrogen bonding with H---N distances 1.640 Å and 1.565 Å respectively. Strong hydrogen bonding exists in isomers **6a** and **3b**. Isomers **3a-3c**, **2a'**, **3a'**, **3b'**, **4b'**, **4c'**, **5a'** and **7b'** shows moderate hydrogen bonding. The difference between the stabilities of corphycenes (**3a-3c** and **3a'-3b'**) and hemiporphycenes (**2a-2c** and **2a'-2b'**) can also to be traced by ring strain, as hemiporphycene is better hydrogen bonded than corphycene. In general the *syn* tautomers have strong hydrogen bonds compare to the corresponding *anti* tautomers. In stability of all the low energy porphyrin isomers is clearly a manifestation of strong NH---N hydrogen bond resulting in short hydrogen bonding distances. Extremely long and unequal H-N-C angles leads to a high energy isomer.

### Central cavity

The four adjacent N-N distances of all the *syn* and *anti* porphyrin isomers are given in Tables 3 and 4. The sum of the four N-N distances of the individual isomers may be taken as a measure of the effective cavity sizes of the porphyrin isomers. These measures give a straightforward indication of the cavity size of the porphyrin isomers. The inner protons were not considering when estimating the cavity sizes as normally complexation is invariably associated with displacement of the protons.

The porphyrin isomer **1** is having large cavity size with a square geometry (2.937Å). In corphycenes, isomers **3b** and **3c** have large N<sub>3</sub>-N<sub>4</sub> distances 4.123 and 4.151 Å respectively. In isomers **4d**, **4e**, **5b** and **5c** the imino proton distances are very large due to more puckering of these isomers. In porphycenes, the isomers with EE form (**4d** and **4e**) have large N<sub>2</sub>-N<sub>3</sub> and N<sub>4</sub>-N<sub>1</sub> distances and isomer **4e** has similar N<sub>1</sub>-N<sub>2</sub> and N<sub>3</sub>-N<sub>4</sub> distances. Isomers **5b**, **5c** and **5d** (N<sub>3</sub>-N<sub>4</sub> distance also large) have large N<sub>4</sub>-N<sub>1</sub> distances range from 4.207 to 4.246 Å this is due to the distortion into bowl-like structure in order to avoid the steric repulsion between the inner CH group. Isomers with [3.0.1.0], [3.1.0.0] and [4.0.0.0] connectivity the N<sub>3</sub>-N<sub>4</sub> varies from 3.098 to 4.589 Å. Like *anti* porphyrin isomers the *syn* porphyrin isomers **4d**, **4e**, **5b**, **5c** and **5d** isomers also have large N<sub>4</sub>-N<sub>1</sub> distances. Isomer **4d** has similar N<sub>4</sub>-N<sub>1</sub> and N<sub>2</sub>-N<sub>3</sub> distances. In isomers [4.0.0.0], which have connectivity with the maximum possible bipyrrrolic linkage, Z isomer and EZ isomer have large N<sub>4</sub>-N<sub>1</sub> distance. Isomers with [3.1.0.0] and [4.0.0.0] connectivity the imino proton distance is less compare to other *syn* porphyrin isomers.

**Table 3.** The adjacent N---N distances and imino proton distances (Å) of *anti* tautomer of porphyrin isomers obtained at B3LYP level using the 6-31G basis set

Struct.	N <sub>1</sub> -N <sub>2</sub>	N <sub>2</sub> -N <sub>3</sub>	N <sub>3</sub> -N <sub>4</sub>	N <sub>4</sub> -N <sub>1</sub>	H-H
<b>1a</b>	2.937	2.937	2.937	2.937	2.208
<b>2a</b>	2.375	2.760	2.897	3.236	2.354
<b>2b</b>	2.646	2.756	-a-	-a-	2.470
<b>2c</b>	2.951	2.574	3.693	2.840	2.448
<b>3a</b>	2.642	2.735	3.555	2.727	2.268
<b>3b</b>	2.793	2.534	4.123	2.691	2.569
<b>3c</b>	2.796	2.684	4.151	2.549	2.744
<b>4a</b>	2.864	2.627	2.864	2.627	2.375
<b>4b</b>	2.823	3.326	2.729	2.887	2.391
<b>4c</b>	-a-	-a-	2.865	2.649	2.576
<b>4d</b>	2.624	4.178	2.565	4.153	3.305
<b>4e</b>	2.590	4.173	2.590	4.173	3.334
<b>5a</b>	2.522	3.257	3.257	2.522	2.010
<b>5b</b>	2.497	2.780	2.695	4.246	3.182
<b>5c</b>	2.472	2.766	3.052	4.376	3.109
<b>5d</b>	2.610	2.601	4.107	4.207	2.755
<b>5e</b>	2.725	2.597	-a-	-a-	3.216
<b>6a</b>	2.451	2.766	3.098	2.758	2.242
<b>6b</b>	2.680	2.650	3.732	2.674	2.254
<b>7a</b>	2.458	2.534	3.660	2.817	2.352
<b>7b</b>	2.620	2.457	4.291	2.772	2.605
<b>8a</b>	2.586	2.606	4.589	2.613	2.635
<b>8b</b>	2.489	2.567	4.267	2.506	2.491

-a- the imidazole ring is inverted.

**Table 4.** The adjacent N---N distances and imino proton distances (Å) of *syn* tautomer of porphyrin isomers obtained at B3LYP level using the 6-31G basis set

Struct.	N <sub>1</sub> -N <sub>2</sub>	N <sub>2</sub> -N <sub>3</sub>	N <sub>3</sub> -N <sub>4</sub>	N <sub>4</sub> -N <sub>1</sub>	H-H
<b>1a'</b>	3.241	2.692	3.158	2.692	2.125
<b>2a'</b>	2.978	2.528	3.284	2.866	1.746
<b>2b'</b>	3.168	2.518	4.012	2.883	2.158
<b>3a'</b>	2.756	2.633	3.623	2.633	2.083
<b>3b'</b>	2.864	2.513	4.104	2.658	2.335
<b>4a'</b>	2.916	2.582	2.867	2.582	2.340
<b>4b'</b>	2.933	3.070	2.821	2.690	2.306
<b>4c'</b>	2.834	3.001	2.885	2.704	2.147
<b>4d'</b>	2.827	3.889	2.732	3.888	2.008
<b>4e'</b>	2.707	3.875	2.750	4.065	2.076
<b>5a'</b>	2.672	2.414	3.396	2.995	1.892
<b>5b'</b>	2.595	2.558	3.047	3.927	1.949
<b>5c'</b>	2.612	2.580	3.113	4.142	2.033
<b>5d'</b>	2.726	2.588	4.115	4.063	2.044
<b>5e'</b>	2.664	2.589	-a-	-a-	2.206
<b>6b'</b>	2.781	2.525	2.745	3.544	2.059
<b>7a'</b>	2.705	2.363	3.003	3.399	1.948
<b>7b'</b>	2.596	2.480	2.923	4.181	1.981
<b>8a'</b>	2.699	2.567	4.662	2.568	1.923
<b>8b'</b>	2.579	2.492	4.198	2.571	1.900
<b>8c'</b>	2.632	-a-	-a-	2.533	2.107

-a- the imidazole ring is inverted.

## Conclusions

The present study reports density functional calculations on a series of *syn* and *anti* tautomeric forms of porphyrin isomers. The relative energy differences seem to critically depend on the length and position of the meso bridges. The isomers [2.1.1.0], [2.1.0.1], [2.0.2.0], [2.2.0.0]

having two  $-(CH)-$  linkages, prefer Z isomer than E isomers. Isomers [2.2.0.0], [3.0.1.0], [3.1.0.0], [4.0.0.0] are destabilized by the presence of severe angle strain in the  $-(CH)_n-$  linkages. The present computational study touches upon a few important aspects of porphyrin chemistry, such as the relative stabilities of tautomers, geometrical isomers. This study provides a good insight about the geometry, energetics and reactivity of various porphyrin isomers and the perturbations that are caused to these isomers upon shuffling hydrogen positions. The variation in number of methine groups drastically alters the stability in these classes of compounds

Several factors, such as angle strain, inner proton repulsion, hydrogen bonding, length of the bridge and the type of geometrical isomerism- E or Z, play important roles in deciding the relative stability ordering of the porphyrin isomers. In  $-(CH)_2-$  linkers the Z forms are more stable than E form due to significant  $\pi$ -delocalization and hydrogen bonding, even in the presence of significant angle strain in it. The E form isomers are distorted into bowl-like structure in order to avoid the steric repulsion between the inner CH group. In trimethine interpyrrole linker E forms are having lower energy than the Z form due to the unstrained bond angles in these isomers. In isomers [4.0.0.0], which have connectivity with the maximum possible bipyrrrolic linkages, Z isomer is having high energy this is due to possibly strained bonds that are directly connect to pyrrole rings.

## Acknowledgements

Authors would like to thank Dr. J. S. Yadav, Director, IICT for his constant encouragements and financial assistance to MP.

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IICT communication no. 040903.

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