Theor Chem Acc (2007) 117: 239–245
DOI 10.1007/s00214-006-0142-0

REGULAR ARTICLE

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Computational study of supramolecular bis-porphyrin “molecular tweezers”

Recevied: 23 June 2005/ Accepted: 23 November 2005 / Published online: 22 June 2006

Abstract A computational study of a series of space separated bis-porphyrin “molecular tweezers” using semiempirical (AM1) and DFT (B3LYP and PBE1PBE) methods has been carried out. It was found that polynorbornane bis-porphyrin systems are significantly less rigid than previously thought. The variation of the metal–metal separation distance between the two porphyrin centers does not cause a significant energy change thus enabling these molecules to easily adjust to the optimal coordination distance required for complexation by various bidentate 4-pyridyl ligands inside the cavity of these “tweezers”.

Keywords DFT calculations · AM1 calculations · Porphyrins · Complexation · Supramolecular

1 Introduction

Supramolecular systems [1] possessing various flexible and semi-flexible linkers between two porphyrin rings have been synthesized and employed in host-guest studies [2–19]. These bis-porphyrin molecular tweezers are particularly interesting due to their ability to complex various ligands [20,21] and fullerenes [22–25]. Molecular modeling of related systems, at both semiempirical and DFT levels by Klärner has revealed the ability of these molecules to act as supramolecular hosts by acting as molecular tweezers, clamps and clips for synthetic receptors [26,27]. Other authors have also reported modeling studies of extended, rigid polycyclic systems using semiempirical calculations [28,29] for rigid molecular tweezers [30]. We have shown in previous research that semiempirical AM1 method is suitable for molecular modeling of polycyclic molecules [31,32].

Literature reports have indicated that certain polycyclic structures possessing polynorbornane spacers are not rigid based on 3–21G calculations of their neutral forms and radical cation [33,34]. Our previous experimental work on bisporphyrin tweezers [35] and modeling of rigid, space separated bis-porphyrin supramolecular systems has revealed that these systems have a significant degree of backbone flexibility [36](Fig. 1). In order to examine this problem in detail, here, we report a computational study on the molecular structure and complexation of several bis-porphyrin molecular tweezers. For this purpose, the recently synthetized bis-porphyrin **1** [37,38] possessing a semi-flexible linker with cyclohexene hinges, a rigidly linked bis-porphyrin **2** [39] and model molecules **3–5** (Fig. 2) were calculated at the semiempirical (AM1) level. Due to the size of these molecules, the investigation of their conformational space was performed using the AM1 method, while the energetics of their complexations were further refined by PBE1PBE/3–21G and B3LYP/LANL2DZ methods. For the sake of computational efforts, in all these studies esters and other substituents were removed.

2 Results and discussion

The most important calculated ground-state geometrical parameters of molecules **1–5** are collected in Table 1. Note that the Zn–Zn inter-atomic distance varies from 12.1 to 23.8 Å, depending on the size of the polycyclic spacer

Article 54, *ECCC-10*, April 1-30 2005, http://www.eccc.monmouth.edu

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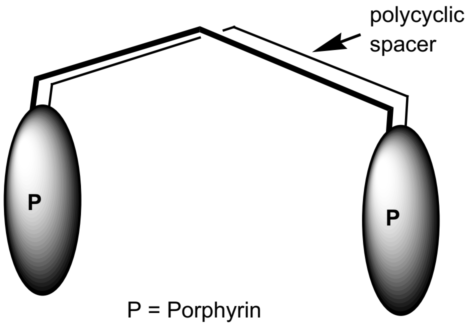

Fig. 1 Schematic diagram of bisporphyrins separated by polycylic spacer

Table 1 AM1 Zn–Zn separation (Å) and interplanar porphyrin–porphyrin angle Ψ (°) between the two porphyrin rings for molecules **1–5**

Molecule	1	2	3	4	5
Zn–Zn	17.417	23.77	22.81	15.12	12.14
Ψ	12.1	41.5	63.9	34.3	25.4

between the two porphyrin units. The two porphyrin rings are oriented towards each other with an interplanar porphyrin–porphyrin angle Ψ varying from almost parallel (Ψ =12.1° in molecule **1**) to Ψ=63.9° in molecule **3** (Fig. 3) [40].

Bending potentials were calculated for molecules **1–5** (by constraining Zn–Zn distances, with 1 Å increments) and these results are depicted in Figs. 4, 5 and 7. Inspection of these graphs reveals very flat bending potentials, with distortions of the molecules by 5–8 Å causing a comparably small change in energy of about 1 kcal mol^{-1} (Fig. 4). These results clearly indicate that despite being constructed of rigid and semi-rigid polycyclic frameworks, these systems are quite flexible and could thus act as molecular tweezers of variable geometries.

A closer examination of the bending potential of molecule **1** (Fig. 5) has shown that there is an unexpected change in energy at a Zn–Zn separation distance of 21 Å . It was found that this behavior is due to the flipping of the porphyrin ring moiety about the cyclohexene ring, changing the structure from a bent to a linear conformer (Fig. 6a).

There are three possible conformers, bent–bent (**1**), bent–linear (**1a**) and linear–linear (**1b**), as depicted in Fig. 6a. The AM1 calculations predict that the linear–linear conformer **1b** is more stable than the linear–bent conformer **1a** by 0.46 kcal mol^{-1} and more stable than bent–bent conformer **1** by 0.87 kcal mol^{-1} . Finally, the AM1 method predicts a slight preference for **1a** over **1** by 0.41 kcal mol^{-1} . The activation energy for flipping of the model system **1c** → **1d** was calculated to be very low (only 0.30 kcal mol^{-1}) indicating facile conformational flexibility of **1**. The AM1 transition state structure for this process with a single imaginary frequency of vibration ($\nu^{\neq} = 14.6\,\mathrm{cm}^{-1}$) is depicted in Fig. 6c.

These results are in good agreement with the calculations of C_{60} ball-and-chain molecules in which a cyclohexene ring connects the polycylic bridge to the fullerene cage [41]. Here, it was reported that the linear conformer is energetically preferred and that there is also a small estimated energy barrier for their inter-conversion.

In contrast to molecule **1** which possesses a cyclohexene ring hinge, the bending potential of molecule **2** which lacks this flipping ability is symmetrical (Fig. 7).

2.1 Complexation studies

In order to examine host-guest interactions in **1**, we have modeled zinc–porphyrin (ZnP)–pyridine complexes with several pyridyl ligands: viz., pyridine (**6**), 4,4′–bipyridyl (**7**), 1,4-di(4′–pyridyl)benzene (**8**), 1,4-di(4′–pyridyl)pyridazine (**9**) and 1,4-di(4′–pyridyl)-*s*-tetrazine (**10**), as depicted in Fig. 8. The same ligands were also used to model related bis-complexes with bis-porphyrin **1** (as illustrated for the **1@ 9** complex in Fig. 9).

The ideal Zn–Zn distance for complexation of bis-pyridyl ligands **8–10** inside the cavity of our molecular tweezers would be the sum of 11.2 Å (ligand N–N separation) and 2 × 2.2 Å (Zn . . . N_{Py} coordination distance) viz., 15.6 Å. Since the Zn–Zn separation of **1** was calculated to be 17.4 Å for the binding of bis-ligands **8–10** within these cavities, a slight distortion of the host is required, which is, according to calculations discussed in the previous section, a very facile process.

An examination of the results obtained by AM1 calculations has revealed that this method provides quite accurate geometries of these model zinc porphyrin–pyridine complexes. The geometry of the square-pyramidal coordinated zinc atom is calculated to be 0.32 Å out of the porphyrin plane, which is comparable to that found by X-ray determination of zinc porphyrin–pyridine complexes (0.2–0.3 Å) [42]. The AM1 bond lengths and angles of the porphyrin moiety are similar to those of experimental porphyrin structures (Fig. 10).

Selected experimentally obtained bond lengths and torsion angles are collected in Table 2 and compared with AM1 and B3LYP/LANL2DZ calculated Zn_P–pyridyl complexes. Both methods correlate well with available experimental data. Experimental Zn_P–N_1 bond lengths ARE within a range of 2.028–2.091 Å, the average N_1–Zn_P–N_2 bond angles are 88.6°, while the axial Zn_P . . . N_{rmPy} coordination bond lengths vary from 2.097 to 2.285 Å [43–47]. Zn–N bond lengths obtained by the AM1 method were slightly more elongated than experimental values. The other carbon–carbon and carbon–nitrogen bond lengths and angles of porphyrin were in good accord with experimental values. Furthermore, the AM1 Zn_P . . . N_{Py} bond lengths were predicted to be slightly longer than experimentally determined Zn_P . . . N_{Py} bonds in porphyrin complexes. It is also important to note that reported crystal structures show that the zinc–pyridine bonds are not ideally perpendicular to the porphyrin plane, but instead are tilted by about 10° from the normal position. This geometrical feature was modeled correctly by AM1 calculations. Furthermore, the pyridine ring was slightly tipped with respect to the Zn_P–N_{Py} bond; that is, the

Table 2 Selected geometrical parameters for **ZnP@guest** complexes

	XR			AM1					B3LYP/ LANL2DZ				
	XR1[58]	XR2[59]	XR3[60]	**6**	**7**	**8**	**9**	**10**	**6**	**7**	**8**	**9**	**10**
Zn–N_1	2.065	2.068	2.073	2. 082	2.085	2.085	2.083	2. 080	2.104	2.103	2.104	2. 104	2.101
Zn–N_{Py}	2.234	2.171	2.143	2. 246	2.253	2.248	2.257	2. 269	2.237	2.240	2.232	2. 243	2.251
Zn–oop^a	0.29	0.33	0.33	0. 32	0.32	0.32	0.32	0. 32	0.34	0.34	0.32	0. 35	0.33
N_1–Zn – N_2	88.9	88	88.3	88.8	88.5	88.7	88. 6	88.9	87.0	88.7	88.6	88.6	88.7
Zn–N_{Py}–C_{Py}	1.6			1.1	0.3	0. 3	1.6	0.3	0.1	0. 3	0.1	0.5	0.3

Bond distances are given in Å, while angles in° *XR* X-ray structures
^{a}Out of plane deviation of zinc

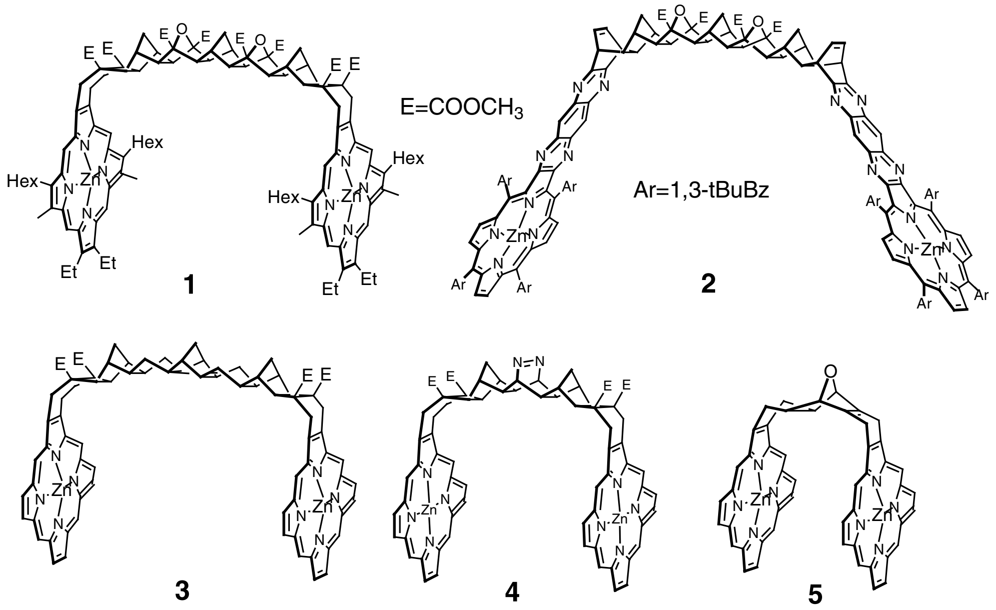

Fig. 2 Bis-porphyrins connected with polycyclic spacers modeled in this study

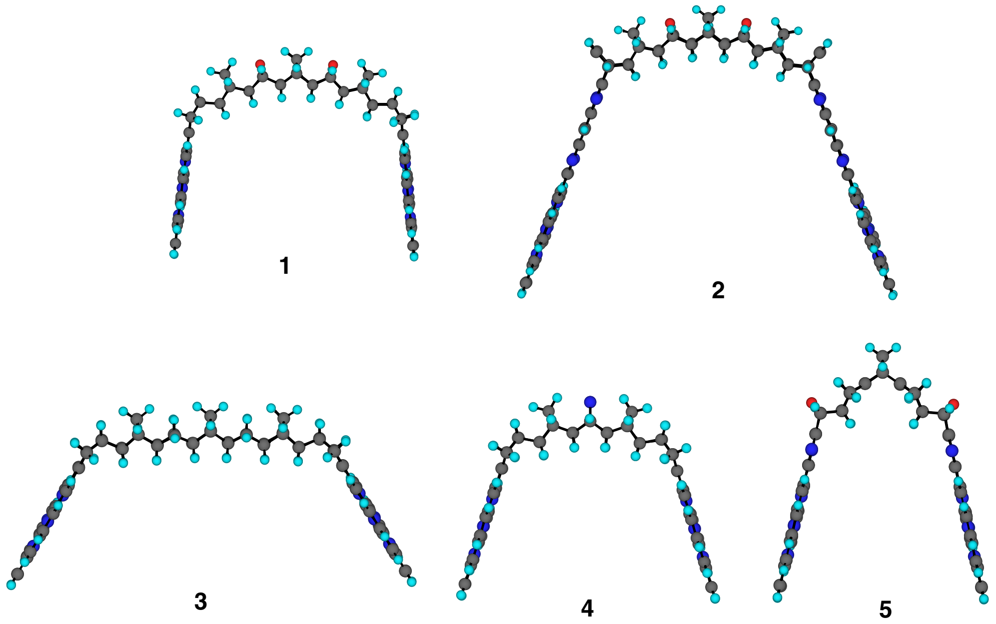

Fig. 3 AM1 optimized structures of **1–5**, side-view

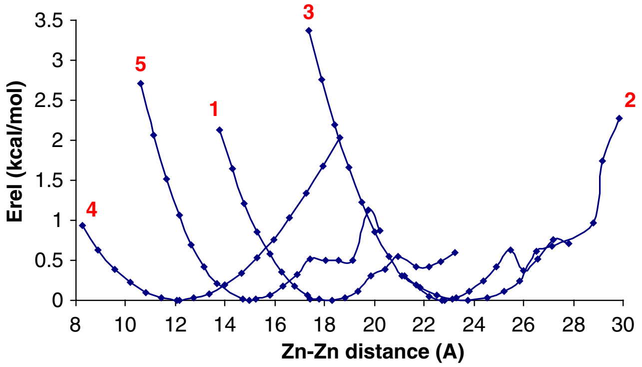

Fig. 4 Comparison of AM1 bending potentials for molecules **1–5**

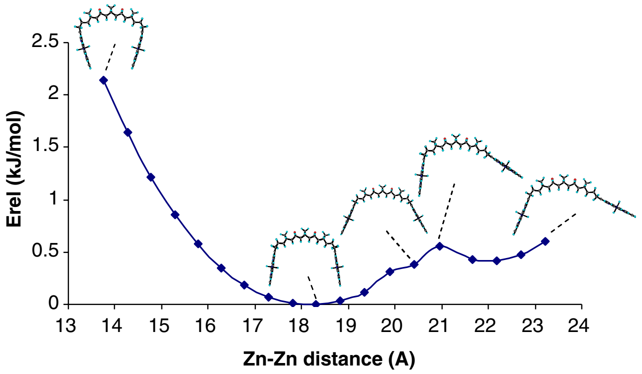

Fig. 5 AM1 bending potential of **1**

plane of the pyridine ring and the $Zn_P \ldots N_{Py}$ bond formed an angle of 182° rather than the expected 180°. This deviation is quite small for calculated **ZnP**@pyridine complexes, but it is much more pronounced for 1@guest complexes (Table 3). The most extensive tilt of the bound pyridine was predicted for the 1@**7** complex (15.3°) and could have been the result of the distortion of bis-porphyrin host **1**. Here, the two porphyrin rings are not parallel but at an angle of 84.1° to each other. The deviation from the ideal coordination angle (90°) caused by the strain and steric hindrance of the pyridyl hydrogen atoms at the α-positions to the nitrogen atom [48] results in weaker binding and is reflected in the longer $Zn_P \ldots N_{Py}$ distance in this complex (2.305 Å). Other complexes have $Zn_P \ldots N_{Py}$ coordination bond lengths comparable to those calculated for **ZnP@Py** complexes (Table 2).

2.2 Energetics of complexation

The supramolecular properties of the bis-porphyrin molecular tweezer **1** were modeled by the incorporation of pyridyl ligands **6–10** within a cavity. Gas-phase binding energies (E_B) were estimated by the difference in energy of the **ZnP@Guest** complexes with optimized energies of pyridyl ligands and the **ZnP** (Table 4). The same computational methodology was used to estimate binding energies for **1@Guest** complexes. In this model, the gas-phase interaction energy of the porphyrin with pyridyl ligands was calculated to be about 2 kcal mol^{-1}. Estimated AM1 binding energies (E_B) of **1@Guest** complexes are generally larger by 1.2 kcal mol^{-1} than those of the model **ZnP@Guest** complexes, indicating stronger binding within a host cavity than for the single-ligated complexes. Binding energies suggest a preference of bis-pyridyl ligands **8–10** to coordinate inside the cavity, rather than outside. This is not the case for pyridine **6**, where the binding energy for inside complexation with **1** is almost the same as for the model porphyrin–Py complex, indicating non-specific binding. Furthermore, for ligand **7**, a positive binding energy of 0.31 kcal mol^{-1} was calculated. This result may be rationalized in terms of the ring strain imposed by complexation with tweezer **1** [49]. The calculated N–N distance of this bis-ligand is much shorter (7.12 Å) than in all other bis-pyridyl ligands studied here (11.22–11.39 Å) and requires larger bending of the polycyclic skeleton of host **1**.

To refine these energetics of complexation, more accurate calculations were performed using PBE1PBE/3–21G and B3LYP/LANL2DZ methods, and the results are summarized in Table 4. Binding energies obtained with these methods are much larger when compared to the AM1 values. The same conclusions can be made from DFT results: binding energies of **1@Guest** complexes are about double those of **ZnP@Guest** complexes indicating specific binding of the guest inside the cavity of **1**. The only exception is pyridine **6**, where non-specific binding is predicted. The smallest E_B was calculated for bipyridyl guest **7**, presumably due to the larger geometrical distortion of molecular tweezers (due to the shortest distance between the two ligating nitrogens in **7**). It is interesting to note that binding energies obtained by DFT methods for **7** are negative, indicating energy stabilization upon complexation. This result is in contrast with AM1 predictions, but in good accord with experimental results, indicating that DFT calculations perform better at estimating the energetics of complexes. Finally, there is a decrease in E_B in the guest series **8–9–10**. Diminished electron density of the pyridyl nitrogens affects the binding ability of ligands [50] which is caused by electron withdrawing nitrogens in the central aromatic ring. This premise was supported by calculations of Mulliken charges at the pyridyl nitrogen atom in ligands **6–10**. They were calculated to be −0.189 (**6**), −0.183 (**7**), −0.186 (**8**), −0.179 (**9**) and −0.169 (**10**), respectively. The electron density of the pyridyl nitrogen atom in **6** is the largest, and accordingly, the calculated binding energy for **ZnP@6** complex is greater than any other ligand studied here.

3 Computational details

All geometry optimizations were carried out with semi-empirical calculations using the AM1 Hamiltonian [51], PBE1PBE/3–21G [52,53] and B3LYP methods [54,55] with LANL2DZ basis set [56], as implemented in the *Gaussian 03* suite of programs [57] on *Octane* Silicon Graphics workstations and

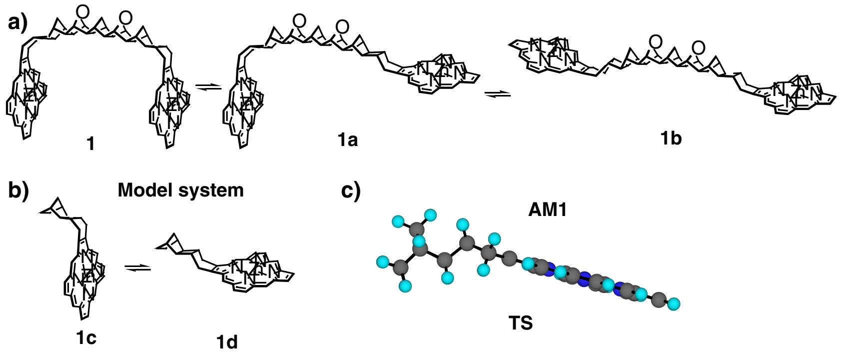

Fig. 6 **a** Flipping of the cyclohexene ring in **1**; **b** model system **1c**→**1d**; **c** AM1 **1c**→**1d** transition state structure

Table 3 Selected geometrical parameters for **1@guest** complexes

	AM1					B3LYP/LANL2DZ				
	6	**7**	**8**	**9**	**10**	**6**	**7**	**8**	**9**	**10**
Zn–N_1	2.088	2. 090	2.083	2.082	2.081	2. 102	2.105	2.103	2.109	2.101
Zn–N(Py)	2.247	2.305	2. 257	2.267	2.283	2.241	2. 262	2.230	2.247	2.256
Zn–oop[a]	0.287	0.320	0.322	0. 288	0.289	0.333	0.296	0. 299	0.323	0.277
N_1–Zn–N_2	88.9	87.9	89.3	88.9	89.3	88. 7	89. 0	88.5	88.9	90.0
Zn–N(Py–C	0.9	9.2	4.4	2. 2	4.7	0.0	8.7	2. 8	1.0	0.0

Bond distances are given in Å, while angles in°

[a] Out of plane deviation of zinc

Table 4 Binding energies (E_B) for complexes (kcal mol^{-1})

	AM1		PBE1PBE/3– 21G		B3LYP/LANL2DZ	
Guest	**ZnP**@Guest	**1@Guest**	**ZnP**@Guest	**1@Guest**	**ZnP**@Guest	**1@Guest**
6	−2.48	−2.62	−31.0	−30.9	−13.8	−13.3
7	−2.13	0.31	−30.5	−57.1	−13.5	−23.6
8	−2.31	−3.37	−30.9	−59.6	−13.8	−26.2
9	−1.91	−2.54	−30.4	−59.2	−13.3	−25.6
10	−1.46	−1.68	−29.6	−58.1	−12.8	−24.6

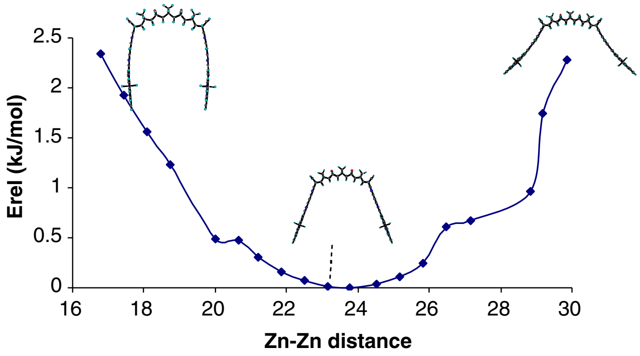

Fig. 7 AM1 bending potential of **2**

the Isabella computer cluster (24 dual processor HP ProLiant BLP20p nodes with Intel Xeon 2.8 GHz, 32 dual processor Dell 1850 1U nodes with Intel Xeon 3.4 GHz and 24 dual processor Pyramid GX28 nodes with AMD Opteron 248).

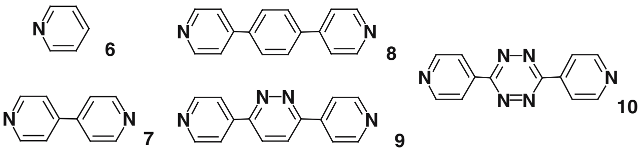

Fig. 8 Pyridine ligands calculated in this study

4 Conclusion

The AM1 method is suitable for calculations of the molecular structure of polycyclic zinc–porphyrins and their pyridine complexes. It was found that all calculated porphyrins possess very shallow energy potentials, enabling distortion of the polycyclic skeleton to adjust for coordination with bis-pyridyl ligands. Binding energies for bis-ligand complexation obtained at AM1 and DFT levels indicate that preferential mode of coordination is inside the cavity of the molecular tweezers discussed here.

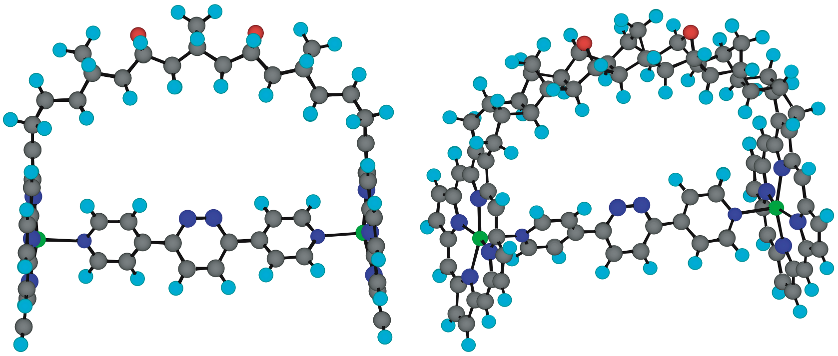

Fig. 9 AM1 model of the **1@9** complex

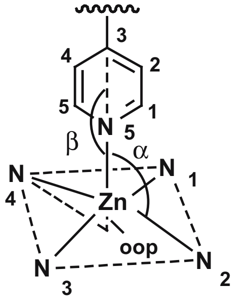

Fig. 10 The idealized C_{4v} geometry of the square–pyramidal coordination group in porphyrin complexes

Acknowledgements The University of Wollongong is gratefully thanked for a visiting fellowship (2004–2005) awarded to D.M. We thank also Mr. Mario Vazdar for technical help and valuable discussions during the preparation of this manuscript. The University of Zagreb is thanked for access to the Isabella computer cluster.

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