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# Structure and Binding Energies of the Porphine Dimer

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## Abstract

Density functional theory optimisations with GGA functionals that include an empirical correction term for the dispersion energy (denoted as -D) have been performed for the van der Waals dimer of porphine. Interaction energies have been also obtained with a recently developed double-hybrid functional (B2-PLYP-D) and at the SCS-MP2 level of theory. The preferred conformer is a parallel displaced complex (1.72 Å lateral displacement) with an interplanar distance of 3.27 Å. The orientation (rotation) of the two monomers has only minor effects ( $< 1 \text{ kcal mol}^{-1}$ ) on the binding energy  $\Delta E$ , implying a certain flexibility of mutual movement around the monomer principal axes. The best estimate for  $\Delta E$  is  $-25 \text{ kcal mol}^{-1}$  with B2-PLYP-D. The also investigated T-shaped structures are much higher (about  $15 \text{ kcal mol}^{-1}$ ) in energy. While dispersion contributions are absolutely essential for the binding of all investigated structures, the electrostatic contributions mainly determine the preferred conformations (e.g. displacement vs. rotation).

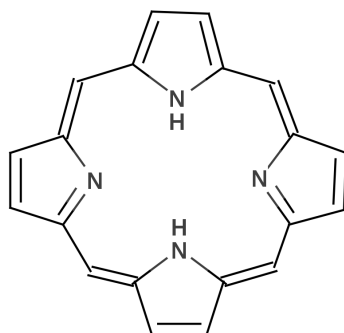
## 1 Introduction

Aromatic functional groups play an important role for the intermolecular interactions between complex molecules, especially biomolecules. Molecules like toluene, azulene or pyridine have permanent electric dipole moments. Electrostatic and dispersion forces usually are of the same order of magnitude and determine the functional role of these groups in cooperative processes such as recognition, ion transport or the formation of two- or threedimensional regular structures[1, 2].

Besides the nucleic acids that are information carriers in the very sophisticated recognition machinery of DNA replication, porphyrines are among the most important polar aromatic molecules in biochemistry. For decades they have been subject to research, mainly owed to their outstanding photophysical properties. The metal binding capability and the redox behaviour of these complexes make porphyrines an essential component of

larger biomolecular systems that are involved in energy transfer processes (haemoglobin, chlorophyll). There are numerous reports in the literature about linking porphyrines to supramolecular assemblies by different binding strategies: (a) complexation of the central metal atom by substituents at the porphyrin ring, see e.g. in refs [3, 4] or (b) hydrogen bonds or non-covalent interactions between substituents, e.g. in ref [5].

The free base porphine **1** is the root compound of all porphyrines. It has  $D_{2h}$  symmetry[6] which has been confirmed with theoretical methods including electron correlation treatment. Hartree-Fock calculations predict a  $C_{2v}$  symmetric structure [7, 8]. It is found less often in nature than its metalated derivatives, e.g. in hematoporphyrin. However, it is increasingly used as part of artificial supramolecular systems and nanostructures, e.g in ref [9]. The so-called  $\pi$ - $\pi$ -stacking between porphine monomer units is often mentioned as one of the interactions that have significant influence on structure formation. For recent reviews on the theoretical treatment of such dispersion dominated interactions using wave function methods see refs.[10, 11, 12, 13]. Nevertheless, there are no reports about assemblies of porphyrines without the presence of other interactions (between substituents) that bring the aromatic planes into a parallel orientation.



Chemical structure of free base porphine **1**

Presently, density functional theory (DFT) is the quantum chemical method that is most applicable for larger chemical systems with sufficient energetic accuracy. Unfortunately, the weak, long-ranging dispersion forces are not recovered by the most popular functionals[14]. One of the problems is that for typical van der Waals distances ( $> 3\text{\AA}$ )

1 the electron density between the fragments is very small and the density deformations  
2 due to bonding are rather unspecific and thus difficult to handle by a density functional.  
3 Several attempts have been made to overcome this deficiency, the most simple of which is  
4 the use of a sum of atom-pairwise dispersion terms depending on  $R_{ij}^{-6}$  and element-specific  
5  $C_6$  coefficients. It is usually turned off at short interatomic distances  $R_{ij}$  by a damping  
6 function[15, 16] in order to avoid double counting effects of electron correlation. In the  
7 most widely used approach[17], the total amount of dispersion correction ( $E_{vdW}$ ) is simply  
8 scaled by a parameter ( $s_6$ ) which allows a specific adaption to different density function-  
9 als and even semiempirical methods[18]. The DFT-D approach is computationally simple  
10 and applicable to a large variety of chemical systems[19] with sufficient accuracy[20].

11 Although much is known about the physical and chemical properties of free porphine and  
12 its metal complexes, only few reports are available about the intermolecular potential of  
13 the dimer ( $(\mathbf{1})_2$ ) without a central metal atom. In the solid state structure of  $\mathbf{1}$ , a parallel  
14 displaced (PD) dimer is found with an interplanar distance of 3.41 Å. It further interacts  
15 with its neighbour pairs through additional CH- $\pi$  contacts.[21, 6]

16 A porphine dimer has also been found in a specifically designed cage complex involving  
17  $\pi$ - $\pi$  interactions with the host[22]. Here the distance between the monomers is found to  
18 be 3.51 Å. Figure 1 sketches the orientation of  $(\mathbf{1})_2$  in the solid state and in the mentioned  
19 supramolecular complex.

20 { Put Figure 1 here }

21 In one early report, attractive intramolecular interactions between two porphine moieties  
22 in a macrocyclic ring were found and proven by anisotropy effects of the aromatic system  
23 on the second ring. An estimation of the dimer binding energy of (zinc) porphyrine by  
24 analysing the thermodynamics of metal complexation vs. stacking interaction gave  $-11.5$   
25  $\pm 2.4$  kcal mol $^{-1}$  [23]. The authors predicted a parallel displaced porphyrine dimer as  
26 the minimum structure by a combined electrostatic multipole/dispersion model[24]. To

1 the best of our knowledge, a detailed quantum chemical study including analysis of the  
2 porphine intermolecular potential has not been published so far. This is the topic of this  
3 contribution.  
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## 10 2 Technical Details

11 All calculations have been performed with the Turbomole program suite[25], with the  
12 additional dispersion correction term in both energy and gradient calculations.[15] A  
13 triple- $\zeta$  AO basis[26] was used in conjunction with three sets of polarisation functions  
14 on all atoms as implemented in the Turbomole basis library (TZV(2df,2dp) or TZVPP).  
15 Detailed convergence studies in refs.[15, 17, 20, 27] have shown that such basis sets provide  
16 results quite close to the basis set limit in DFT computations of noncovalently bound  
17 complexes.  
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29 For the full geometry optimisations we have used B97-D[17], a modified version of Beckes  
30 semiempirical GGA functional introduced in 1997[28]. The parameters of the GGA had  
31 been reoptimised in B97-D in the presence of the dispersion correction. B97-D van  
32 der Waals complex binding energies are exceptionally good and reach almost CCSD(T)  
33 quality[20]. For comparison of the energies with a second functional, the structures have  
34 also been optimised with the dispersion corrected B-LYP functional[29, 30]. The resolu-  
35 tion of identity (RI) approximation[31, 32] was used for the DFT calculations with B97-D  
36 and B-LYP-D.  
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46 The usual counterpoise correction (CP)[33, 34] for basis set superposition error (BSSE) has  
47 not been included for the DFT-D/GGA binding energies because in our experience, the  
48 BSSE is sufficiently small ( $<5-10\%$  of  $\Delta E$ ) with the triple- $\zeta$  AO basis sets used. Further-  
49 more, BSSE effects have been already accounted for in the DFT-D fitting procedure[15].  
50 Energies were then recalculated with the recently introduced double-hybrid density func-  
51 tional B2-PLYP[35], that contains a perturbative (virtual orbital dependent) contribution  
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2 to the correlation energy. Together with the dispersion correction (B2-PLYP-D, scaling  
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4 coefficient  $s_6=0.55$ ) it yields [36] very accurate energies for non-covalent binding ener-  
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6 gies (MAD=0.3 kcal mol<sup>-1</sup> for the S22 test set of Jurecka et al.[37]), when half of the  
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8 counterpoise correction energy  $\Delta E_{CP}$  is added to the interaction energy  $\Delta E$ .  
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10 We also applied the SCS-MP2 model[38], a recently introduced improved version of stan-  
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12 dard Møller-Plesset perturbation theory in which the correlation energy is partitioned into  
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14 parallel- and antiparallel-spin components which are separately scaled. It provides sig-  
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16 nificantly improved energetics compared to standard MP2 for a wide variety of chemical  
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18 systems often reaching QCISD(T) accuracy and also corrects for the systematic overesti-  
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20 mation of MP2 for van der Waals interactions in unsaturated systems[38, 39, 40, 41, 42].  
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22 SCS-MP2 and B2-PLYP-D calculations also used the RI approximation for the perturba-  
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24 tive step[43]. The SCS-MP2 energies were CP corrected since these interaction energies  
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26 include the largest BSSE of all the methods that were used. In the SCS-MP2 and B2-  
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28 PLYP-D computations we used the optimised B97-D geometries.  
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32 In order to understand the intermolecular binding in more detail, we performed energy  
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34 decomposition analyses (EDA) at the B97-D/TZV(2df,2dp) level of theory to distinguish  
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36 the various contributions to the total binding energy. The EDA has proven to give de-  
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38 tailed information about the nature of chemical bonding[44, 45, 46] as well as recently for  
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40 the interactions in DNA base pairs[47]. Besides the dispersion term from the empirical  
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42 correction, interaction energies are partitioned into contributions from Pauli exchange  
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44 repulsion ( $E_{ER}$ ), electrostatic ( $E_{ES}$ ) and induction ( $E_{Ind}$ ) interactions, the three terms  
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46 that comprise the (uncorrected) DFT binding energy  $E_{DFT}$ .  
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### 51 3 Results and Discussion

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55 We were primarily interested in the mutual orientation of the two rings with respect to  
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57 each other. The conformation of parallel (stacked and displaced) dimers can be described  
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1 by three geometric parameters: the distance  $r$  between the two molecule planes, the  
2 displacement  $d$ , the length of the vector between the centres of the monomers, projected  
3 on the plane of the (lower) ring, and  $\beta$ , the angle of rotation of the upper monomer around  
4 its centre, measured by the angle between the NH-HN lines of both monomers, projected  
5 on the plane of one monomer.  
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12 To proceed in a systematic manner, eight structural motifs have been taken into account  
13 (see figure 2), derived from the possible dimers of e.g. benzene: (a) sandwich (SW) com-  
14 plexes **A-C** with  $d=0$  and various rotation angles of the two dimers against each other,  
15 (b) parallel displaced (PD) complexes with parallel (**D,E**) or orthogonal (**F**) N-H bond  
16 directions and (c) T-shaped dimers **G** and **H** with one monomer perpendicular to the  
17 second.  
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27 At this point one must of course take into account that hydrogen tautomerisation, convert-  
28 ing e.g. **A**  $\rightarrow$  **B**, is a comparatively fast process that has been studied both in solution and  
29 in the solid state[48]. For clarity, we will talk of conformers of  $(\mathbf{1})_2$  throughout the text,  
30 although the conformers can also be regarded as tautomers and conformational changes  
31 are slower than hydrogen exchange.  
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40 The corresponding interaction energies are gathered in table 1 and shown graphically in  
41 figure 3. We discuss mainly the B97-D values which are representative also for other  
42 dispersion corrected GGAs (e.g. B-LYP-D) and finally comment on the methodological  
43 dependence of the results.  
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50 { Put Figure 2 here }

51 { Put Table 1 here }

52 { Put Figure 3 here }

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2 An EDA analysis of the energy contributions to the binding energy has been performed for  
3 all complexes with the B97-D functional. The results are given in table 2 and will also be  
4 discussed in the following. It must be pointed out at this stage that none of the complexes  
5 is bound at the pure DFT level, i.e., without the dispersion correction. Although for B97-  
6 D this may be a misleading finding because the parameters in the functional have been  
7 optimised in the presence of the dispersion correction[17], this also holds for B-LYP (data  
8 not shown) and very likely for many other GGAs including hybrids. It should also be noted  
9 that the contributions found in the EDA analysis are not independent: electrostatic and  
10 dispersion contributions are often counterbalanced by higher Pauli exchange repulsion  
11 energies. Interpretation of the data in table 2 (and this holds for most other energy  
12 partitioning schemes as well) must therefore be done with caution, although the results  
13 for a series of different conformations seem to provide meaningful information.

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Geometry changes of the monomers upon complex formation are negligibly small ( $< 10^{-2}$   
Å). It is thus certainly justified in future studies to employ frozen monomer geometries.

{ Put Table 2 here }

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The three sandwich dimers **A-C** with the second monomer placed directly above the  
first, are all higher in energy than displaced complexes **D-F**. Not surprisingly, the fully  
eclipsed dimer **A** is the least stable of the three. **C** is more favourable than the  $D_{2h}$ -  
and  $D_{2d}$ -symmetric SW dimers. A shorter distance (3.42 Å) is found between the two  
monomers in **C**. Both eclipsed isomers have longer interplanar distances (**A**: 3.67 Å, **B**:  
3.62 Å), reflecting the smaller attraction between the monomers. This is underscored  
by the EDA analysis which indicates that although **C** suffers from a larger exchange  
repulsion, stabilising electrostatic and dispersion contributions are substantially larger  
than in **A** and **B**.  $E_{ER}$  and  $E_{vdW}$  increase with opposite sign as the interplanar distance  
decreases: thus rather the more favourable electrostatic and induction contributions are  
determining the preference of **C** over the two eclipsed conformers **A** and **B**.

1 Comparing **A** with **B**, rotation of one monomer by 90° around the central axis of **A** (or H  
2 tautomerisation) increases the electrostatic stabilisation despite the also higher dispersion  
3 contribution.  
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8 None of the three sandwich complexes are minima on the intermolecular potential energy  
9 surface: displacement of one monomer in small steps (0.1 Bohr) parallel to the second  
10 molecule leads to lower energies irrespective of the direction. The presence of a structural  
11 motif similar to **C** in the host-guest complex (figure 1, right) has therefore to be explained  
12 by geometrical constraints imposed by the rigid cage.  
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15 Starting from either **A** or **B**, parallel displacement of the monomers leads to the two  
16 dimers **D** and **E** ( $C_{2h}$ -symmetry) or **F** with  $C_S$ -symmetry, respectively.  
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19 All three PD isomers are found within an energy range of less than 1 kcal mol<sup>-1</sup> with  
20 all methods used here - an indication of the very flat energy surface that describes the  
21 movement of the projected centre of the second around the centre of the first monomer.  
22 This flexibility is also reflected in the solid state structure (figure 1, left), where the dimer  
23 conformation is half-way between the stationary points **D** and **E**. Optimisation without  
24 geometry restriction (B97-D/TZV(2df,2dp)) starting from the reported dimer geometry  
25 in the crystals of **1** gives the dimer **E**. Thus, the specific packing in the crystal is presum-  
26 ably responsible for the distortion from the 'better' conformation.  
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43 The displacement of the monomers against each other is similar for all three PD conformers  
44 (1.72-1.80 Å) and leads to the assumption that there is a 'sombbrero-hat' potential surface  
45 for the shift in the plane. In the solid state, (**1**)<sub>2</sub> shows a displacement of 1.6 Å, in good  
46 agreement with our optimised values.  
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51 The monomer-monomer distance is also very similar for the three conformers **D-F** (3.26-  
52 3.27 Å) and about 0.15 Å shorter than in the solid state structure. The distance is also  
53 shorter than for the less stable sandwich dimers. The EDA analysis reflects the better  
54 binding in (absolutely) larger  $E_{ER}$  and  $E_{vdW}$  contributions. These are larger than those  
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2 of **A-C**, but vary less (within  $1.3 \text{ kcal mol}^{-1}$ ). It is rather the electrostatic part of the  
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4 total binding energy that determines the relative energies of the PD complexes: **E** and **F**  
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6 are preferred over **D** by  $0.5 \text{ kcal mol}^{-1}$  in total,  $E_{ES}$  for the two former complexes is by  
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8  $0.9$  and  $1.3 \text{ kcal mol}^{-1}$  larger than for **D**.  
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10 The T-shaped dimers **G** and **H** have a much lower binding energies than the sandwich  
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12 and PD complexes due to their smaller van der Waals interactions. **H** with the methine  
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14 group hydrogens pointing towards the centre of the second ring is preferred ( $\Delta E = -9.7$   
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16  $\text{kcal mol}^{-1}$ ). It has almost half the binding energy of the best PD dimer **F**. Nonpolar  
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18 and polar aromatic molecules show opposite electrostatic potentials above the molecular  
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20 plane and the rim (hydrogen atoms), but there is no large absolute electrostatic and/or  
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22 induction contribution to the binding energies of the two T-shaped complexes (table 2).  
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24 However, the sum of non-dispersion contributions to the bindings energies is larger than  
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26 for the other complexes, leaving **G** and **H** almost bound without the dispersion correction.  
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28 This reflects the general tendency of non-dispersion corrected density functionals to prefer  
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30 CH- $\pi$  over  $\pi - \pi$  arranged structures.  
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34 Finally, we want to discuss the absolute size of the interaction energies as obtained from  
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36 different methods (see table 1 and Fig. 3). Note that the relative energies for the different  
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38 stacked structures and also the absolute values of the T-shape conformers are rather  
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40 similar with all methods. Thus, our conclusions about the most stable conformations are  
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42 not affected by the choice of the theoretical method.  
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45 As pointed out in several reviews before, the  $\pi - \pi$  stacked arrangements are most prob-  
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47 lematic for any theoretical treatment. Although we observe similar trends for the binding  
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49 energies with different methods here as for e.g. the benzene dimer, due to the much larger  
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51 size of the porphine dimer systematic errors are strongly amplified. This already explains  
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53 why the methods differ for the interaction energy of e.g. **F** within about  $6 \text{ kcal mol}^{-1}$ .  
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55 Recent studies showed that the B2-PLYP-D method is most accurate for vdW complexes  
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57 and non-covalent interactions in general[36]. With the suggested 50% counterpoise cor-  
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1 rection, we arrive at final best estimate for  $\Delta E$  of  $-25 \text{ kcal mol}^{-1}$  for dimer **F** with a  
2 conservative error estimate of  $\pm 3 \text{ kcal mol}^{-1}$  (about 10%). This value is in very good  
3 agreement with the CP-corrected SCS-MP2 value of  $-26.0 \text{ kcal mol}^{-1}$ . To the best of our  
4 knowledge, corrected B2-PLYP-D and SCS-MP2 binding energies have never deviated  
5 by more than 10% from reliable references. At the complete basis set limit, SCS-MP2  
6 energies have been shown to be of high accuracy ( $< 3 \%$ )[41, 42].  
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10 The B97-D and B-LYP-D interaction energies are smaller by about 20% but errors of this  
11 size can be expected for large unsaturated  $\pi$ -systems because the atomic  $C_6$  coefficients  
12 used are molecule independent.  
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## 22 4 Conclusions

23 Dispersion corrected DFT and wavefunction SCS-MP2 calculations have shown that the  
24 van der Waals dimer of porphine prefers a stacked, parallel displaced geometry with two  
25 monomers rotated against each other by  $90^\circ$ . The energy surface is flat and would allow  
26 movement (single and mutual rotations) of the monomers within a certain displacement  
27 range. The measured binding enthalpy for intramolecular dimerisation of two zinc por-  
28 phyrines is by about  $15 \text{ kcal mol}^{-1}$  smaller than our best estimation for the binding energy  
29 ( $-25 \pm 3 \text{ kcal mol}^{-1}$ ). However, the solvent effect in the experiments is not covered by our  
30 gas phase calculations. As we have shown for the example of anthracene[49], the loss  
31 of solvent-solute interactions must be taken into account if self-aggregation is considered  
32 for larger aromatic molecules in solution. In any case we suggest the porphine dimer as  
33 the next standard test system (the successor of the benzene dimer) for quantum chemi-  
34 cal methods that accurately try to include all relevant non-covalent interactions. While  
35 dispersion contributions are absolutely essential for the binding of all investigated struc-  
36 tures, the electrostatic contributions mainly determine the preferred conformations (e.g.  
37 displacement and rotation) or preferred tautomers of **(1)**<sub>2</sub>.  
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Table 1: Binding energies  $\Delta E$  of porphine dimers with different density functionals and SCS-MP2 in kcal mol<sup>-1</sup> (TZV(2df,2dp) AO basis).

	BLYP-D	B97-D	B2-PLYP-D <sup>[a]</sup>	SCS-MP2 <sup>[b]</sup>
Stacked dimers				
<b>A</b> ( $D_{2h}$ )	-11.7	-13.5	-15.3 (-17.0)	-17.7 (-23.6)
<b>B</b> ( $D_{2d}$ )	-12.8	-14.5	-16.6 (-18.3)	-19.0 (-25.1)
<b>C</b> ( $C_2$ )	-17.2	-18.3	-22.1 (-24.3)	-24.6 (-32.5)
Parallel displaced dimers				
<b>D</b> ( $C_{2h}$ )	-19.3	-20.0	-24.4 (-26.7)	-25.6 (-34.1)
<b>E</b> ( $C_{2h}$ )	-19.9	-20.5	-24.9 (-27.2)	-25.8 (-34.4)
<b>F</b> ( $C_2$ )	-20.0	-20.6	-25.0 (-27.3)	-26.0 (-34.7)
T-shaped dimers				
<b>G</b> ( $C_{2v}$ )	-8.0	-8.4	-8.6 (-9.2)	-7.3 (-9.6)
<b>H</b> ( $C_s$ )	-9.4	-9.7	-10.3 (-11.0)	-9.1 (-11.9)

<sup>[a]</sup> Counterpoise corrected ( $\Delta E + \frac{1}{2}\Delta E_{CP}$ , in brackets uncorrected) energies.

<sup>[b]</sup> Counterpoise corrected ( $\Delta E + \Delta E_{CP}$ , in brackets uncorrected) energies.

Figure 1: Dimer motifs of porphine in the solid state of **1** (left) and as guest in a supramolecular complex (right).

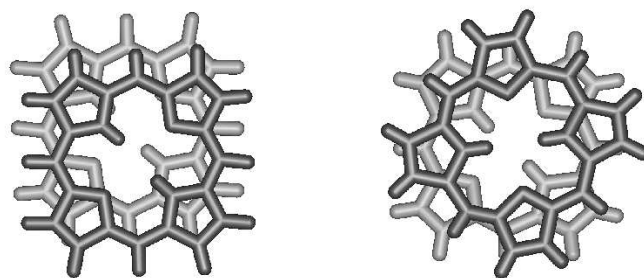


Table 2: Energy decomposition analysis (B97-D/TZV(2df,2pd)) of porphine dimers. Given are the Pauli exchange-repulsion, classical electrostatic, induction and dispersion contributions to the binding energy in kcal mol<sup>-1</sup>.  $E_{DFT}$  denotes the uncorrected DFT interaction energy. Interplanar distances<sup>a</sup> and displacement length<sup>b</sup> in Å

Dimer	$E_{ER}$	$E_{ES}$	$E_{Ind}$	$E_{DFT}$	$E_{disp}$	Total $\Delta E$	$r_{dim}$	$d$
<b>A</b>	22.1	-6.1	-3.2	12.8	-26.4	-13.6	3.67	0.0
<b>B</b>	24.2	-8.1	-3.3	12.8	-27.5	-14.7	3.62	0.0
<b>C</b>	39.4	-16.8	-5.6	17.0	-35.5	-18.5	3.42	0.0
<b>D</b>	51.7	-24.3	-8.2	19.2	-39.4	-20.1	3.26	1.72
<b>E</b>	52.5	-25.2	-8.6	18.8	-39.4	-20.6	3.26	1.80
<b>F</b>	53.0	-25.6	-8.5	18.9	-39.7	-20.8	3.27	1.72
<b>G</b>	11.9	-6.7	-4.1	1.0	-9.5	-8.5	7.45	0.0
<b>H</b>	13.6	-6.6	-4.5	2.5	-12.4	-9.9	7.03	0.0

[a] distance between a plane spanned by three nitrogens of one dimer to the centre of the second monomer as defined by the geometric centre of the four nitrogens

[b] distance of the second centre to the norm of the plane spanned by three nitrogens of one dimer moved to the centre of the first monomer.

Figure 2: Investigated porphine dimer motifs A-H.

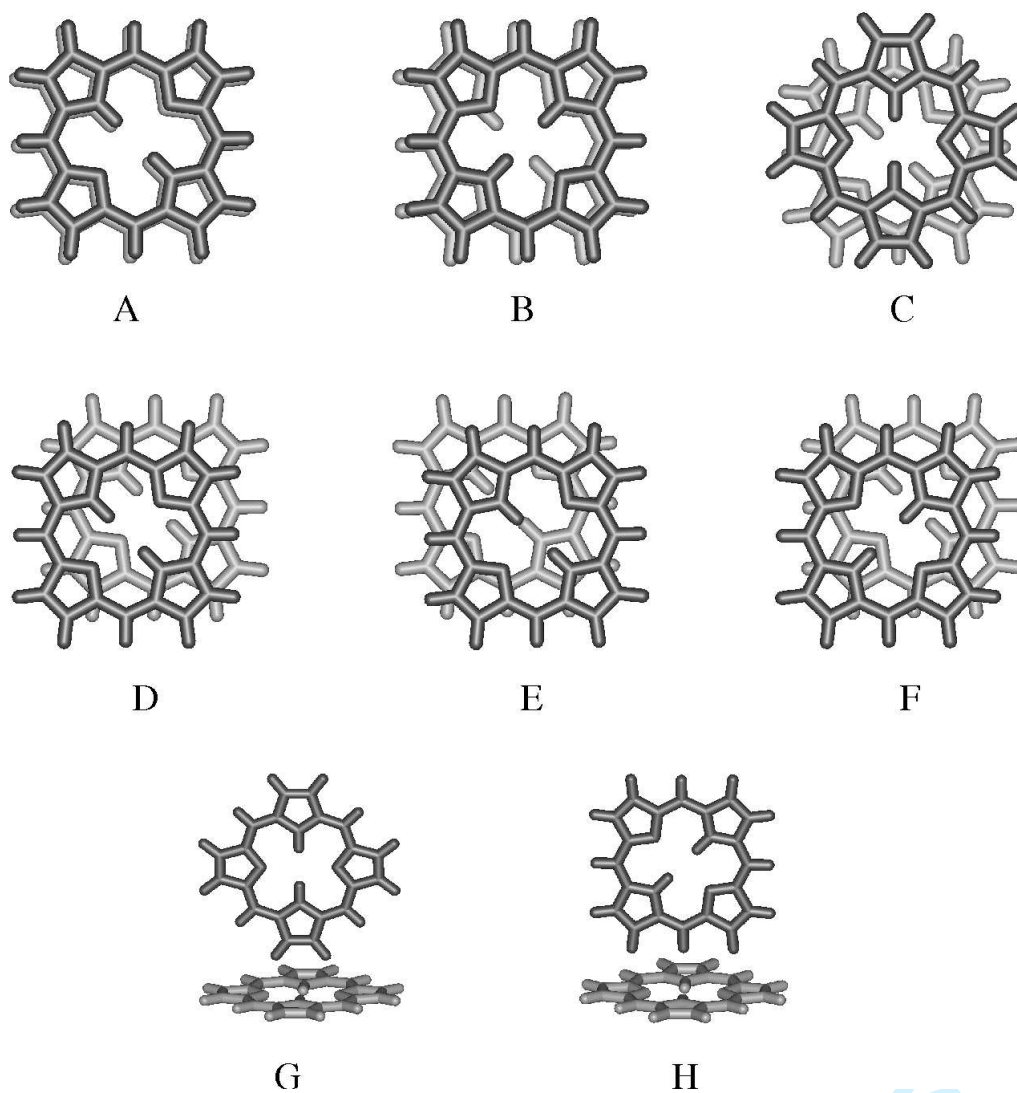
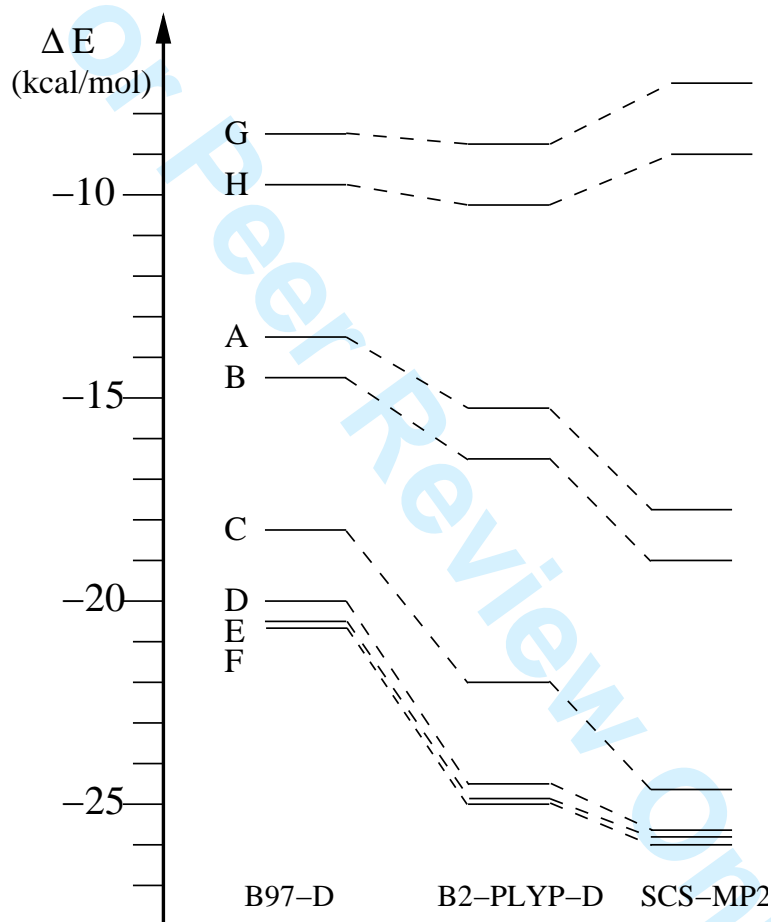
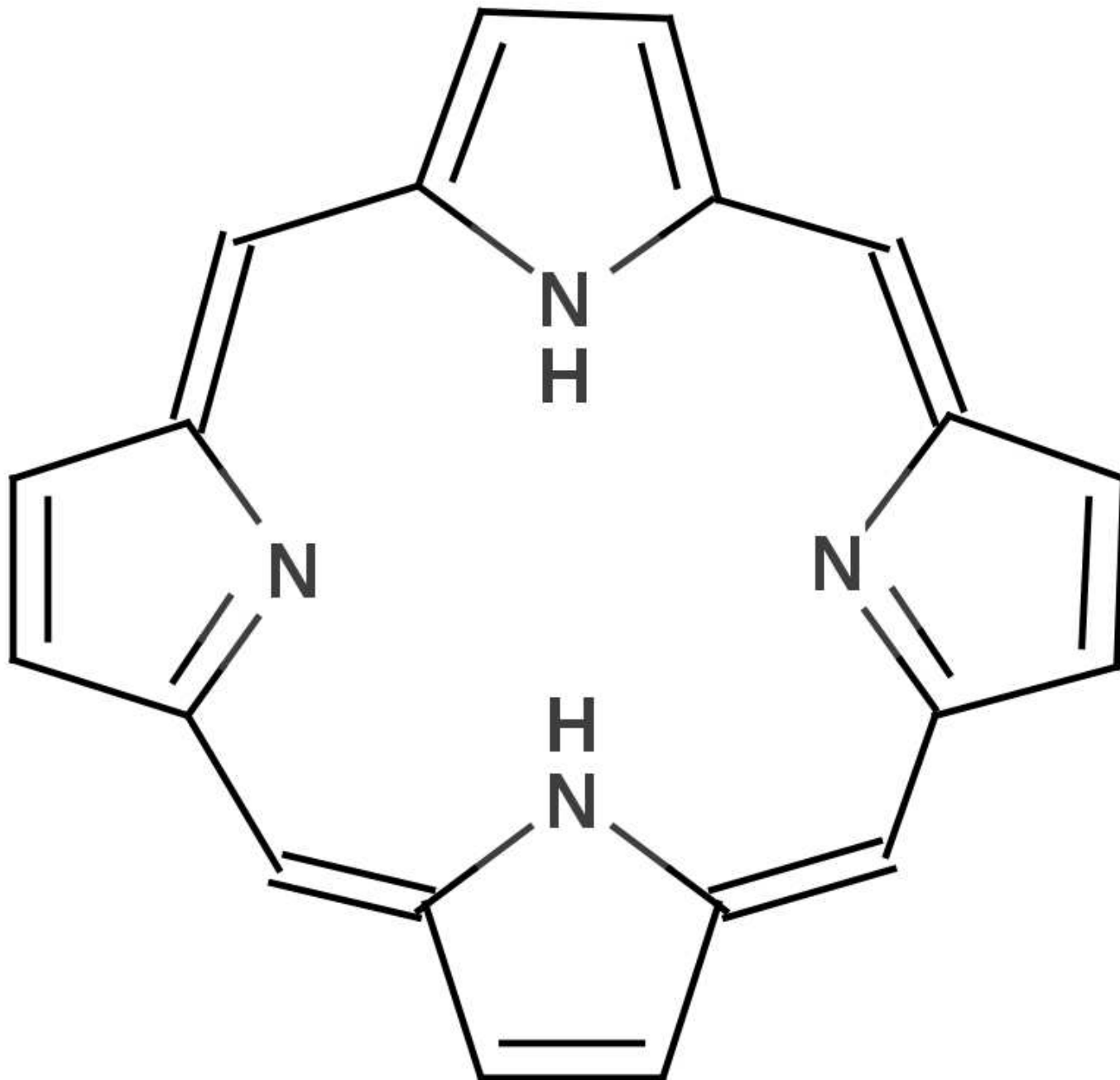


Figure 3: Comparison of porphine dimer binding energies  $\Delta E$  with B97-D, B2-PLYP-D and SCS-MP2 for conformers A-H



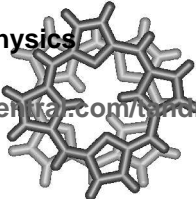


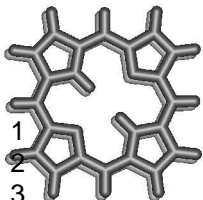
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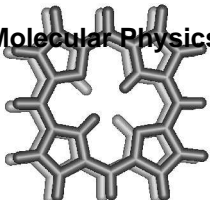
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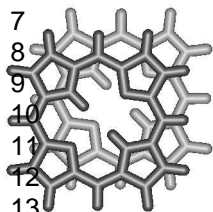
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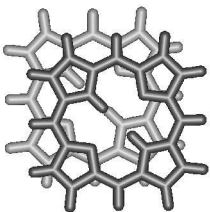
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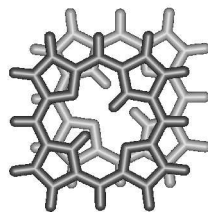
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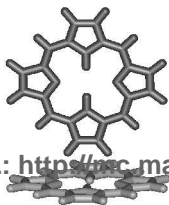
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E



F



G



H

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