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Applicability of the ^{1}H NMR chemical shifts computed by the ab initio/GIAO-HF methodology to the study of geometrical features of Zn-porphyrin dimers

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Abstract—Several porphyrin dimers have been newly designed and synthesized to construct assemblies with 1,4-diazabicyclo[2.2.2]octane (DABCO) as a bidentate binding ligand. Semi empirical (AM1) and ab initio calculations have been used to study the assemblies generated by the organization of dimers and DABCO, including the computation of ^{1}H NMR complexation-induced chemical shifts using the ab initio/GIAO methodology. The diagnostic capacity of the theoretical method has been applied to explain experimental results and geometrical features of the complexes.

Supramolecules containing metalloporphyrins have been widely used in host–guest chemistry.[1] Metalloporphyrins are excellent binding blocks for the construction of large multicomponent architectures due to their stability and facile synthesis. Significant developments in the construction of oligometalloporphyrins supply a large variety of new compounds with interesting potential use in electron transfer.[2] For example, multiporphyrin arrays can be used as photon funnels,[3] molecular wires,[4] switches,[5] etc.

Several synthetic strategies have been employed to bring together porphyrin systems, for instance, a variety of porphyrin ensembles has been constructed covalently, where the porphyrin units are linked through spacers.[6] More recently, self-assembly strategies have been reported to obtain metalloporphyrin oligomers linked noncovalently by hydrogen bonding and coordination via ligands.[6] Zinc-porphyrins are often used as building blocks to create receptors with a range of cavity shapes and sizes. The strategy of this chemistry is based on the essential Zn–N recognition event.[7]

The interplay between theory and experiment in the field of NMR spectroscopy has been very fruitful in many respects,[8] especially for the elucidation of molecular structures and for a better understanding of chemical binding. Therefore, the computation of chemical shift is an ideal link between theory and experiment. Applications of chemical shifts calculations have been reviewed several times focusing on several aspects of the calculations.[9] The NMR chemical shifts of the nuclei in a molecule are determined to the overall geometry and to structural parameters as bond lengths or specific conformations.

We have recently designed, synthesized and studied several Zn-porphyrin dimers (**1a**–**c**) with different geometrical features (Fig. 1), depending on the *ortho*-, *meta*- or *para*-substitution.[10] Their dissimilar behavior to form assemblies with DABCO was studied experimentally by means of UV–vis and ^{1}H NMR spectroscopy and theoretically using semiempirical calculations.

We have recently demonstrated the capability of the theoretical method ab initio/GIAO at the HF/6-311G*//HF/3-21G level of theory to reproduce accurately the characteristic changes in the ^{1}H NMR chemical shift signals of several ligands caused by the proximity of the porphyrin π system upon binding.[11] In this work we attempt to illustrate how this method

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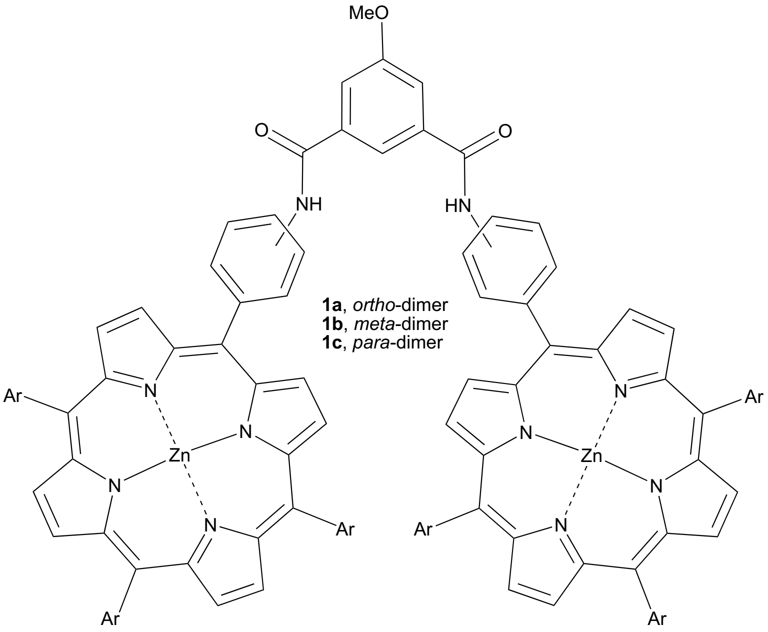


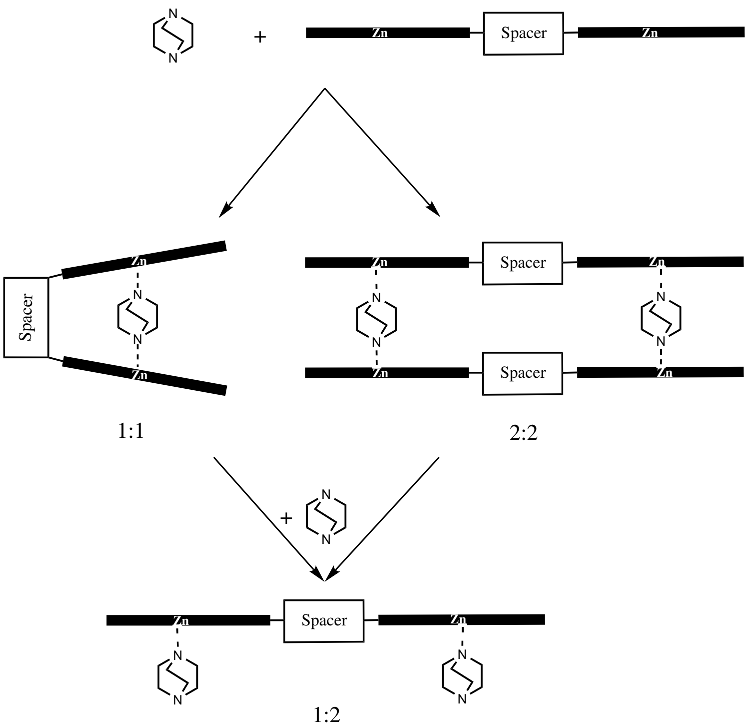
Figure 1. Porphyrin dimers **1a**–**c**.

can be used to understand and elucidate the dissimilar behavior of dimers **1a**–**c** when forming complexes with DABCO and, consequently, simplify the experimental work. Experimentally, an important effort is required (UV–vis and NMR titrations, fitting procedures, etc.) to establish the formation of different Zn-porphyrin dimer/DABCO assemblies, like 1:1, 2:2, 1:2, etc. Each assembly has characteristic geometrical requirements, usually determined by the spacer and the stoichiometry. Clearly, the complexation-induced chemical shift of the protons of DABCO is influenced by the geometry of the complex. In an ideal sandwich complex of two separate Zn-porphyrin systems and one DABCO, the two porphyrin systems are disposed in a completely parallel arrangement and the ring-current effect on the DABCO protons and the complexation-induced field are maximum. When the two Zn-porphyrins are linked by a spacer, they usually cannot reach the ideal sandwich conformation, specially in intramolecular complexes, and the complexation-induced shift is reduced in comparison with the ideal case. In this work we take advantage of this, and just analyzing the ^{1}H NMR spectra of the **1a**–**c** complexes with DABCO and comparing them with the computed ^{1}H NMR complexation-induced field, we can infer the geometrical characteristics of the two porphyrin rings and whether they are forming an intra or intermolecular assembly with DABCO (see Scheme 1).

Semiempirical calculations were carried out at the restricted Hartree–Fock (RHF) level using the AM1[12] method, as implemented in MOPAC-93 package.[13] The geometry of all structures was optimized and further refined by minimization of the gradient norm to less than 0.1 kcal/Å deg by means of the eigenvector following routine (EF).[14] No side chains were attached to the porphyrins evaluated in this study in order to keep the size of the calculation approachable. No symmetry constrains were imposed. Ab initio calculations were done by means of the GAUSSIAN 98 program[15] using the 3-21G basis set at the HF level. GIAO calculations were performed according to the reported method[16] at HF/6-311G*//HF/3-21G level. It is generally accepted that GIAO/DFT methods give better results than GIAO/HF, however, for these systems previous studies have demonstrated that reliable quantitative results are obtained at this level of theory.[11] Chemical shifts were determined by comparisons with the ^{1}H NMR isotropic shifts computed for tetramethylsilane at the same level.

First of all, we have computed the dependence of the complexation-induced field of the DABCO protons upon the angle (α) of the two porphyrin rings (see Fig. 2) by means of the GIAO-HF/6-311G*//HF/3-21G methodology. The change in DABCO chemical shift when it is bound between the two porphyrins is simply the sum of the shifts induced by the two ring currents, as it has been described before.[17] An interesting linear relationship ($r^2 = 0.98$) is found between the orientation angle and the $\Delta\delta_{\max}-\Delta\delta$ difference, where $\Delta\delta$ represents the complexation-induced chemical shift. In these systems the $\Delta\delta$ is very significant because the DABCO methylene protons are affected by the ring-current effect of two porphyrin systems. The data are summarized in Table 1. The $\Delta\delta$ is maximum (represented by $\Delta\delta_{\max}$) when both porphyrin planes are parallel ($\alpha = 0°$) and it is reduced as the value of α increases and consequently the $\Delta\delta_{\max}-\Delta\delta$ difference increases.

Experimentally, we have demonstrated[10] that addition of DABCO to a $CHCl_3$ solution of either porphyrin dimer **1a** or **1b** induces the formation of **1a** and **1b** into 1:1 sandwich complex (see Scheme 1 and Fig. 3). Curiously, the destruction of the 1:1 complex by addition of an



Scheme 1. Schematic representation of the 1:1 and 2:2 intra and intermolecular complexes of Zn-porphyrin dimers with DABCO.

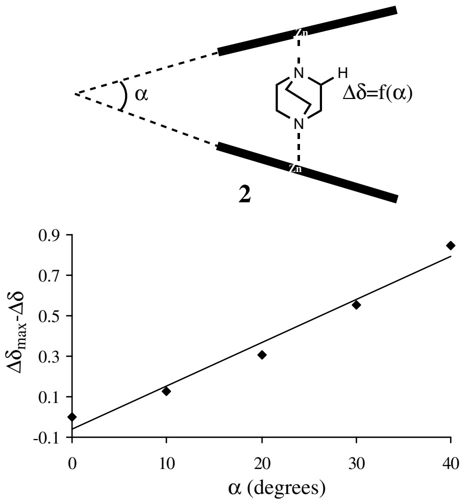


Figure 2. Plot of the regression between the angle defined by the two N_4 planes of both porphyrins in degrees and the complexation-induced shift of the DABCO hydrogen atoms in ppm computed for **2**.

Table 1. Calculated and experimental ^{1}H NMR chemical shifts (δ), complex-induced chemical shifts ($\Delta\delta$) and $\Delta\delta_{max}-\Delta\delta$ difference of the DABCO protons at different values of α

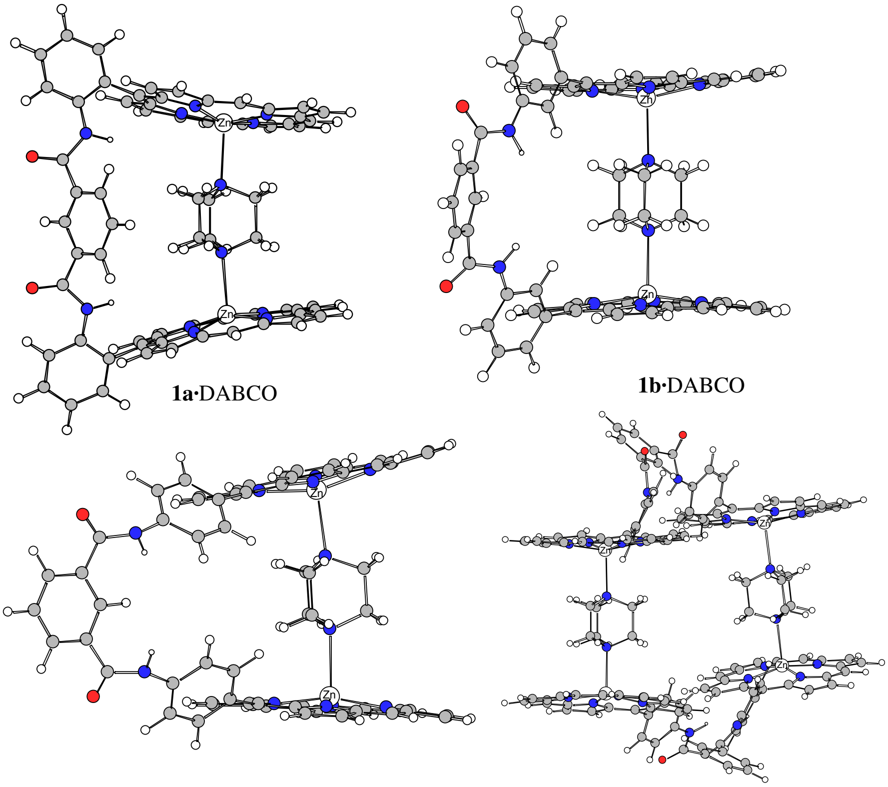
Compound	GIAO/6-311G*//HF/3-21G				Experimental	
	AS[a]	δ[b]	$\Delta\delta$	$\Delta\delta_{max}-\Delta\delta$	δ[b,c]	$\Delta\delta$
TMS	32.77	0	—		0	—
DABCO	30.44	2.31	—		2.80	—
2 (‖)	39.05	−6.30	8.61	0	−5.20	8.00
2 (10°)	38.82	−6.17	8.48	0.13	—	—
2 (20°)	38.74	−5.99	8.30	0.31	—	—
2 (30°)	38.49	−5.74	8.05	0.56	—	—
2 (40°)	38.10	−5.45	7.76	0.85	—	—

[a] Absolute shielding.
[b] Relative to TMS.
[c] In $CDCl_3$ at 20 °C.

excess of DABCO to form the 1:2 complex is considerably more favorable for dimer **1a** than **1b**. In fact the destruction of the 1:1 sandwich complex of **1b** does not start until more than 4000 equiv of DABCO are added. In contrast to **1a** and **1b** dimers, DABCO induces the formation of the **1c** dimer into a 2:2 multicomponent assembly, which is stable in a wide range of DABCO concentrations (see Scheme 1 and Fig. 3).

Theoretically, the existence of 1:1 sandwich complexes of all dimers **1a**–**c** are possible, however, the **1c**·DABCO 1:1 sandwich complex, which is not observed experimentally, is high in energy, probably because the amido groups are very distorted with a high degree of pyramidalization of the nitrogen atoms. The geometries of the three 1:1 complexes are shown in Figure 3. The optimized structure of the 2:2 assembly of dimer **1c** and DABCO is also shown in Figure 3. The angle of the porphyrin systems obtained from the AM1-optimized geometries are present in Table 2.

The different behavior of dimers **1a**–**c** when forming complexes with DABCO can be rationalized using the information obtained by means of (i) the theoretical study combining the computed ^{1}H NMR chemical shifts and the geometries of the optimized complexes, and (ii) the experimental ^{1}H NMR chemical shifts of the DABCO protons upon complexation. Dimer **1a** presents *ortho* substitution which prevents the formation of a



1a·DABCO **1b**·DABCO

1c·DABCO **1c**$_2$·DABCO$_2$

Figure 3. AM1-optimized structures of 1:1 DABCO·**1a**–**c** complexes and the **1c**$_2$·DABCO$_2$ assembly.

Table 2. Experimental ^{1}H NMR chemical shifts (δ) and complex-induced chemical shifts in ppm for complexes **1a**–**c** with DABCO and the reference compound **2**, and the corresponding angle (α, degrees) obtained using the regression of Figure 2

Compound	δ	$\Delta\delta$	$\Delta\delta_{max}-\Delta\delta$	α (°)	α (AM1) (°)
2 (‖)	−5.20	8.00	0	0 (‖)	0 (‖)
1a-DABCO	−4.41	7.21	0.79	39.8	44.1
1b-DABCO	−4.70	7.54	0.46	23.4	18.5
1c-DABCO	−4.98	7.78	0.22	15.1	10.0

2:2 assembly, however, it can reach a conformation that allows the formation of a 1:1 sandwich complex with DABCO. Experimentally,[10] at μM concentration, this complex starts to be destroyed by addition of 25 equiv of DABCO to form the 1:2 complex. The experimental $\Delta\delta$ of the **1a**·DABCO complex is 7.21 ppm, which corresponds to an 'experimental angle' of 39.8° using the regression of Figure 2. This value agrees well with the observed in the AM1-optimized structure of the 1:1 sandwich complex (44.1°). Dimer **1b** presents *meta*-substitution that, similarly to dimer **1a**, also prevents the formation of a 2:2 assembly with DABCO. Nevertheless, it can easily adopt a conformation to form a 1:1 sandwich complex with DABCO. In this case, the **1b**·DABCO complex is more stable than **1a**·DABCO because it cannot be destroyed to form the **1b**·DABCO$_2$ complex until more than 4000 equiv of DABCO are added. The experimental $\Delta\delta$ of the DABCO protons upon complexation is 7.54, indicating that the angle between both porphyrin rings in the complex is 23.4°. This angle also agrees with the computed angle of 18.5° obtained from the AM1-optimized structure. The difference in the angle between the 1:1 complexes of dimers **1a** and **1b** explains the difference in stability and in the complexation-induced chemical shifts. Finally, the **1c** dimer presents *para*-substitution and, in this case, it is geometrically plausible the formation of a 2:2 assembly, in fact it is observed experimentally and can be demonstrated by using tedious ^{1}H NMR and UV–vis titrations and fitting procedures.[10] Using the regression of Figure 2 and the optimized structure this result can be easily corroborated. The observed $\Delta\delta$ of the DABCO protons is 7.78 ppm, the highest value observed for the **1a**–**c** dimer complexes. This $\Delta\delta$ corresponds to an experimental angle between both porphyrins of 15.1°, which agrees with that obtained from the optimized structure of the 2:2 assembly (10.0°). The **1c**·DABCO 1:1 complex is shown in Figure 3. Geometrically, the **1c** dimer cannot easily adopt a conformation that permits the formation of the 1:1 complex. The amido groups in the complex are very distorted and the nitrogen atom has a high degree of pyramidalization. The 1:1 complex is 23.9 kcal/mol higher in energy than the corresponding 2:2 assembly. In addition, the angle (α) obtained from the optimized structure of the **1c**·DABCO complex is 24.1°, approximately 10° higher than the value obtained from the experimental $\Delta\delta$, indicating that the 2:2 assembly formation is preferred over the 1:1 complex.

In summary, we have shown that the theoretical calculations of ^{1}H NMR chemical shift and the complexation-induced shift using the ab initio/GIAO methodology are useful for prediction purposes, even in systems where the ^{1}H NMR signals experience large ring-current-induced shifts. Finally, we have found a linear relationship between the angle of the porphyrin rings in sandwich complexes and the computed complexation-induced shift. This relationship allows us to estimate the 'experimental' angle of different porphyrin dimers using the experimental chemical shifts and rationalize the different behavior of the dimers.

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