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Subporphyrinoid Systems: A Theoretical Study of the Effects of the Diheteroatom Substitution in Pyrrole Subunits and of the Nature of the Bridging *Meso* Linkages

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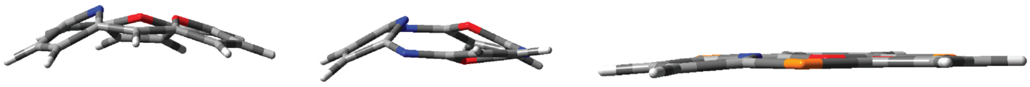

A theoretical study of the geometry, the electronic structure, the electronic absorption spectra, and ^{1}H and ^{13}C NMR spectra of the [14]subporphine(1.1.1)-hydroxyboron(III) complex, free-base subporphyrin, and its dioxygen and dithio pyrrole substituted derivatives using CH, N, and P as bridging *meso* linkages was performed at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) theory level. The geometrical structure of these systems is mainly determined by the internal area delimited by the *meso* atoms and the α-carbon atoms of the pyrrolic rings, and by the number and nature of the atoms located on this area. All the hydroxyboron subporphyrins and dioxo and dithio subporphyrins with CH *meso* connectors display a conical shaped geometry. The presence of strong repulsions between the atoms on the central zone of the remaining systems provokes a correlative tilting of one of the three rings with loss of the conical shape with important consequences on spectroscopic properties. A particularly interesting case is the dioxosubporphyrin with P connectors in which the large area of the central zone determined by these connectors allows for an almost planar geometry that endows it with special features. The molecules presenting a tilted ring display weak absorption bands. Generally, the intensity of the bands moderately increases when the geometry is cone shaped. The dioxo heterosubporphyrins with CH (conical shape) and P (almost planar) connectors present strong absorption bands. ^{1}H and ^{13}C chemical shifts clearly reflect the effect of geometry distortion provoked by the repulsion among the atoms of the central area of the system indicating a deep perturbation of the π system of the molecules.

1. Introduction

Subporphyrinoid systems constitute a family of very interesting molecules because of their promising applications in chemistry, physics, and materials sciences.[1-3] Since the first synthesis of subphthalocyanines by Meller and Ossko[4] in 1972 these molecules have attracted much attention and are the best known subporphyrinoids. Subporphyrazines have been synthesized and characterized in 2005[5] and their porphyrinic counterparts, tribenzosubporphyrins and subporphyrins, have been synthesized and characterized more recently.

In 2006, the first synthesis and characterization of tribenzosubporphyrins as their boron(III) complexes[6] and the first synthesis of a *meso*-aryl subpyriporphyrin with a boron-free structure were reported.[7] More recently, the first synthesis and spectroscopic study of some novel *meso*-aryl subporphyrins as their hydroxyboron(III) complexes have been achieved.[8,9] Also the synthesis of a series of hydroxyboron(III) complexes of *meso*-aryl-substituted subporphyrins and

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[1] Torres, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2834.

[2] Claessens, C. G.; González-Rodríguez, D.; Torres, T. *Chem. Rev.* **2002**, *102*, 835.

[3] Kobayashi, N. In *The Porphyrin Handbook*; Kadish, K. K. M., Smith, R. G., Eds.; Academic Press: San Diego, CA, 2000.

[4] Meller, A.; Ossko, A. *Monatsh. Chem.* **1972**, *103*, 150.

[5] Rodríguez-Morgade, M. S.; Esperanza, S.; Torres, T.; Barberá, J. *Chem.—Eur. J.* **2005**, *11*, 354.

[6] Inokuma, Y.; Kwon, J. H.; Ahn, T. K.; Yoo, M. C.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 961.

[7] Myśliborski, R.; Latos-Grażyński, L.; Szterenberg, L.; Lis, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3670.

[8] Kobayashi, N.; Takeuchi, Y.; Matsuda, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 758.

[9] Takeuchi, Y.; Matsuda, A.; Kobayashi, N. *J. Am. Chem. Soc.* **2007**, *129*, 8271.

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the study of their structures and large substituent effects on their electronic properties have been reported.[10−15]

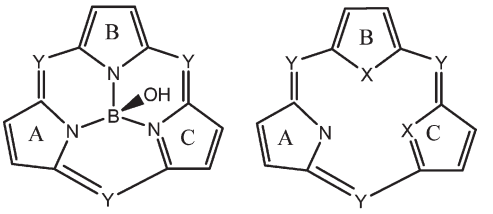
These boron-containing macrocyclic systems are very important from both basic and applied viewpoints constituting a benchmark for investigating the inherent properties of the subporphyrin core as well as promising chromophores.[1,6,8−16] X-ray diffraction analyses have shown that all these genuine ring-contracted porphyrins adopt a nonplanar cone-shaped conformation, which makes them particularly interesting in supramolecular chemistry.[1,6,10,13,16] The NMR spectra of these compounds reveal strong diatropic ring-current effects associated with aromaticity suggesting the presence of a 14π-electron aromatic core.[6,10] Thus, these macrocycles constitute a fascinating example of nonplanar aromaticity and present unique spectral and electronic features.

Although the accomplishments achieved so far in subporphyrinoid chemistry are very important, further work in this field is still necessary. It has been remarked the importance of investigating issues such as the tolerance of heteroatom replacements in the pyrrole subunits, and the effect of varying bridging *meso* linkages.[1] As theoretical studies could help obtaining a deeper understanding of these points, in this paper we present a theoretical study of the geometry, the electronic structure, the electronic absorption spectra, and ^{1}H and ^{13}C NMR spectra of [14]subporphine(1.1.1)-hydroxyboron(III) complex, free-base subporphyrin, and its dioxygen and dithio pyrrole substituted derivatives using CH, N, and P as bridging *meso* linkages (see Scheme 1).

2. Computational Methods

We performed geometry optimizations in the gas phase with the Gaussian03 program[17] using the DFT method through the B3LYP hybrid functional[18−20] with the 6-31G(d) basis set.

SCHEME 1. Ring Naming and Substitution Pattern for the Studied Subporphyrins



Y = CH, N, P

X = NH, O, S

In previous work, this theory level proved to be adequate for studying this kind of systems.[21−23] Vibrational frequencies were calculated for all the studied structures at that theory level characterizing all of them as minima on the corresponding Potential Energy Surfaces. Electronic energies, electronic absorption spectra, and ^{1}H and ^{13}C NMR spectra were calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) theory level. Electronic absorption spectra were evaluated by using the Time Dependent TD-DFT method as implemented in Gaussian.[24] For the evaluation of NMR chemical shifts we used the GIAO (Gauge-Independent Atomic Orbital) method.[25−27] An NBO analysis[28] was also performed at the B3LYP/6-31G(d) theory level. Nucleous-independent chemical shifts (NICS)[29] have been calculated at the subporphyrins center and at the ring critical points of electron density with use of the GIAO method at the B3LYP/6-311+G(2d,p) theory level, using the Gaussian03 program.

3. Results and Discussion

In Figures 1−3 we present the optimized geometries of all the subporphyrinoid systems studied here containing CH, N, and P *meso* connectors, respectively. Table 1 displays the electronic energy, the dipole moment, and some geometrical features of all the systems. Tables 2−4 collect the absorption and NMR (^{1}H and ^{13}C) spectra for the molecules with CH, N, and P *meso* connectors. Finally, Table 5 shows the NICS calculated at the center of the ring critical points of the electron density of the three 5-membered constituent rings and at the middle of the central area for all the studied systems

The geometrical structure of the studied systems is mainly determined by the internal area delimited by the *meso* atoms and the α-carbon atoms of the pyrrolic rings, and by the number and nature of the atoms located in this area (see Figures 1−3). All the hydroxyboron subporphyrins, **CSPBOH**, **NSPBOH**, and **PSPBOH**, present a conical geometrical structure whose apex is shaped by the approximately tetrahedral four bonds around the B atom. None of them have been synthesized yet but we can compare some geometrical parameters of **CSPBOH** with those reported for the corresponding tribenzosubporphyrin system.[6] Our

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(10) Inokuma, Y.; Yoon, Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 4747.

(11) Inokuma, Y.; Easwaramoorthi, S.; Young Jang, S.; Kim, K. S.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4840.

(12) Inokuma, Y.; Easwaramoorthi, S.; Yoon, Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 12235.

(13) Shimizu, S.; Matsuda, M.; Kobayashi, N. *Inorg. Chem.* **2009**, *48*, 7885.

(14) Sakamoto, R.; Saito, S.; Shimizu, S.; Inokuma, Y.; Aratani, N.; Osuka, A. *Chem. Lett.* **2010**, *39*, 439441.

(15) Glasovac, Z.; Vazdar, M.; Margetić, D. *Croat. Chem. Acta* **2009**, *82*, 63–70.

(16) Inokuma, Y.; Osuka, A. *Dalton Trans.* **2008**, 2517.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*, Revision B.04; Gaussian, Inc., Wallingford, CT, 2004.

(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(19) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785.

(21) Delaere, D.; Nguyen, M. T. *Chem. Phys. Lett.* **2003**, *376*, 329.

(22) Campomanes, P.; Menéndez, M. I.; Cárdenas-Jirón, G. I.; Sordo, T. L. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5644.

(23) Campomanes, P.; Menéndez, M. I.; Sordo, T. L. *J. Porphyrins Phthalocyanines* **2007**, *11*, 815.

(24) Wolinski, K.; Hilton, J. F.; Pulay, P.. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(25) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028.

(26) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(27) Dodds, J. L.; McWeeny, R.; Sadlej, A. J. *Mol. Phys.* **1980**, *41*, 1419.

(28) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1998**, *88*, 899.

(29) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. J. R. V. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

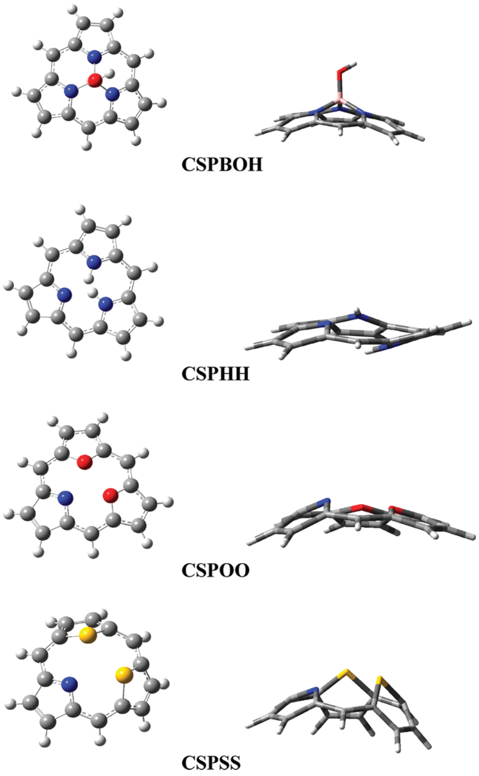

FIGURE 1. Minimum energy structure of subporphyrins with *meso* C linkages. Although no symmetry restriction has been imposed when optimizing these structures, **CSPBOH**, **CPSOO**, and **CSPSS** present approximate C_s symmetry within 0.01 Å precision, and **CSPHH** C_1 symmetry.

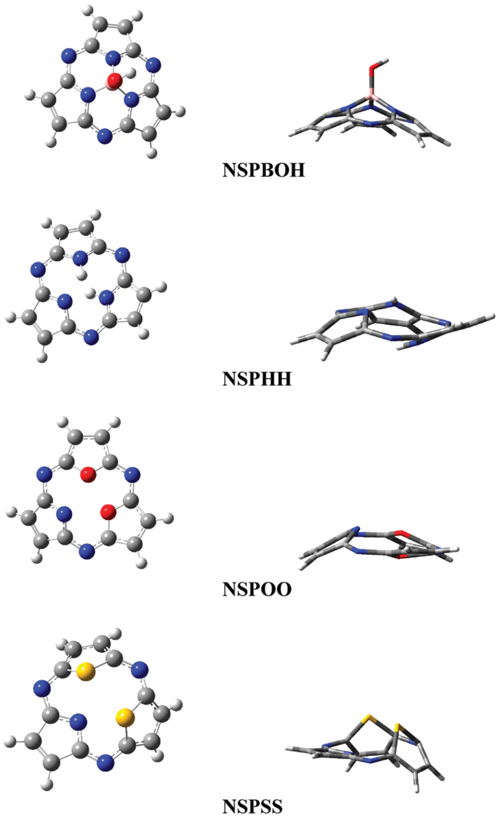

FIGURE 2. Minimum energy structure of subporphyrins with *meso* N linkages. Although no symmetry restriction has been imposed when optimizing these structures, **NSPBOH** and **NSPSS** present approximate C_s symmetry within 0.01 Å precision, and **NSPHH** and **NSPOO** C_1 symmetry.

computational results render average B−N (1.511 Å) and B−O (1.411 Å) bond lengths very similar to those in the larger system (1.51 Å and 1.45 Å, respectively). NBN average angles are about 4° larger in our system.

Evidently, the size of the central area depends on the bond length of the *meso* bonds. As the C−N *meso* bonds are shorter than the C−C ones, 1.345 Å vs 1.412 Å, we found that **NSPBOH** presents a cone depth clearly larger than that of **CSPBOH**, 1.75 Å vs 1.47 Å. (See Table 1; Cone depth is defined as the distance from the mean plane of the six β-carbon atoms of the pyrrole rings to the B atom, in parentheses in the table. To be able to compare the cone depth with molecules not containing the BOH fragment we also defined a cone depth as the distance from the mean plane of the six β-carbon atoms of the pyrrole rings to the barycenter of the three central atoms pertaining to the three pyrrolic rings.) On the other hand, as the C−P bond length (1.764 Å) is larger than the C−C one, the cone depth in **PSPBOH** is only 0.96 Å with the three pyrrole rings practically on the same plane (see Figure 3 and Table 1).

In contrast with the hydroxyboron systems, in the free base subporphyrins the presence of two H atoms on the central area determines such an important repulsion between them that the conical shape geometries are lost (see Figures 1−3). In effect, in the three free base subporphyrins studied one of the pyrrolic rings containing an N−H bond (C ring in Scheme 1) is tilted from the cone conformation so that the N−H bond is located beneath the plane defined by the α-carbon atoms pointing toward the β-carbon atoms of the other two rings (see Figures 1−3). This tilting is larger the smaller the central area, so that the H atom is further underneath the α-carbon plane in **NSPHH** (∼0.9 Å) than in **CSPHH** (∼0.7 Å) and in **PSPHH** (∼0.5 Å).

When the two NHs are substituted by two oxygen atoms the subporphyrin with CH *meso* linkages (**CSPOO**) presents a conical shaped geometry characterized by a cone depth of 0.83 Å. This distance is quite similar to the corresponding one in **CSPBOH**. When N atoms are used as *meso* connectors, however, the geometry of the oxygen heterosystem, **NSPOO**, is not conical shaped but one of the furane rings is tilted toward the β-carbon atoms of the other two remaining rings. Interestingly, when the *meso* connectors in the dioxoheterosubporphyrins are Ps, **PSPOO**, the geometry of the molecule is almost planar. As we will see below, this geometrical conformation determines some interesting spectroscopic features for this system.

When the two NHs in free base subporphyrin are substituted by two sulfur atoms the subporphyrin with CH *meso* linkages, **CSPSS**, presents a conical shaped geometry characterized by a cone depth of 1.76 Å. This distance doubles the corresponding one in **CSPOO** owing to a larger repulsion between the S atoms. When N atoms are used as *meso* connectors the geometry of the sulfur heterosystem, **NSPSS**, is not conical shaped, but at difference with **NSPOO**, now one of the pyrrolic rings is tilted toward the β-carbon atoms of the other two heterorings. It is interesting to note here that we have also located a nonconical shaped structure for **NSPSS** in which the downward tilted ring is one containing

S (analogous to **NSPOO**). However, this last geometry is about 2.5 kcal/mol less stable than the former one. An NBO analysis shows that this energy difference is mainly due to the presence of a couple of lone pair (S)−antibonding (S−C) stabilizing interactions when the two heterorings are pointing upward. Finally, when the *meso* connectors in the dithioheterosubporphyrins are Ps, **PSPSS**, one of the heterorings is tilted toward the β-carbon atoms of the other two. In this case the larger distance between the two S atoms does not allow for the stabilization found in **NSPSS** through the lone pair−antibonding interaction.

Concerning the UV/vis absorption spectra we could compare our results for **CSPBOH** with those reported for *meso*-phenylsubporphyrin.[8] We found a very weak Q-band at about 416 nm (f = 0.01; f = oscillator strength) and a much stronger Soret band at about 318 nm (f = 0.48) comparable to those for *meso*-phenylsubporphyrin at 461 and 373 nm, respectively. For **NSPBOH** we found a band at 420 nm (f = 0.14) and a much weaker band at about 300 nm (f = 0.003) at difference with experimental data for borohydroxy and borochloride subporphyrazines with *n*pr substituents on the β-carbon positions, which present a Q-band at about 500 nm and a Soret band at about 295 nm of similar intensity[5] so, in general, our calculations render energy transitions higher than those experimentally found. From data in Tables 2−4 we see that the intensity of the absorption bands appreciably increases when going from the N connector to the C connector, while when going from that to the P connector a less important variation takes place. This variation of the intensities of the absorption bands is an increase in the case of BOH and free base subporphyrins, and a decrease in the case of heterosubporphyrins. The energy of the bands appreciably increases when going from N connector to C connector, except in the case of oxygen heterosubporphyrins for which a small (6%) diminution takes place. In all the cases the energy of the bands decreases moderately (~20%) when we substitute C connectors by P connectors. These trends could be explained taking into account that the substitution of N connectors by C connectors provokes a diminution of the cone depth, when defined, by reducing the repulsions among atoms in the central zone thus giving rise to more extensive π systems. The exceptional behavior of oxygen supbporphyrins is due to the fact that the two N connectors next to the heteroring C, whose slant breaks the conical shape, are practically in the plane of this ring, whereas in the case of **CSPOO** the C connectors are out of the plane. The general diminution when introducing P connectors is mainly due to the splitting of the molecules π system into pyrrolic π subsystems caused by the P lone pairs, whose higher energy prevents them from fully participating in the delocalization. For every *meso* connector, the energy of the absorption transitions with larger oscillator strength diminishes when going from hydroxiboron systems to the free base systems and to the heterodithio systems, whereas the heterdioxygen systems break this trend by increasing the energy of those bands. Also the oxygen heterosystems represent an exception in this trend so that these molecules display the most intense bands. Therefore, our calculations clearly show that the heterodioxygen subporphyrins studied by us are interesting molecules displaying absorption bands

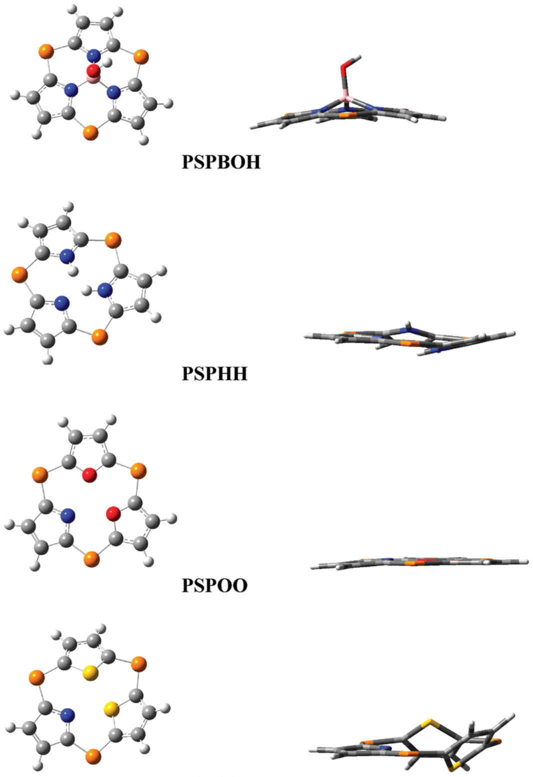

FIGURE 3. Minimum energy structure of subporphyrins with *meso* P linkages. Although no symmetry restriction has been imposed when optimizing these structures, **PSPBOH** and **PSPOO** present approximate C_s symmetry within 0.01 Å precision, and **PSPHH** and **PSPSS** C_1 symmetry.

TABLE 1. B3LYP/6-31G(d) Absolute Electronic Energy (au), Dipole Moment (D), and Cone Depth (Å) for the Studied Subporphyrins

	CSPBOH	**CSPHH**	**CSPOO**	**CSPSS**
electronic energy	−842.305124	−742.602719	−782.319869	−1428.22205
dipole moment	2.970	1.410	3.346	3.773
cone depth	0.84 (1.47)	nonconical	0.83	1.76
	NSPBOH	**NSPHH**	**NSPOO**	**NSPSS**
electronic energy	−890.418102	−790.716232	−830.444061	−1476.339431
dipole moment	2.215	1.415	2.134	1.188
cone depth	1.19 (1.75)	nonconical	nonconical	nonconical
	PSPBOH	**PSPHH**	**PSPOO**	**PSPSS**
electronic energy	−1750.27968	−1650.598238	−1690.294636	−2336.217778
dipole moment	1.363	0.817	1.814	1.666
cone depth	0.39 (0.96)	nonconical	0.07	nonconical

TABLE 2. Most Intense (f = Oscillator Strength) UV/Vis Absorption Bands (nm) and ^{1}H and ^{13}C NMR Chemical Shifts, Relative to TMS at the Same Theory Level, for Subporphyrins with *Meso* C Linkages

	CSPBOH	CSPHH	CSPOO	CSPSS
absorption bands	416.3 (f = 0.01), 318.1 (f = 0.48), 318.4 (f = 0.34), 314.2 (f = 0.18), 265.1 (f = 0.14)	467.1 (f = 0.00), 325.0 (f = 0.27), 320.3 (f = 0.26), 285.3 (f = 0.24), 274.9 (f = 0.22), 355.8 (f = 0.19)	470.6 (f = 0.00), 305.1 (f = 0.71), 296.7 (f = 0.64)	485.4 (f = 0.00), 349.9 (f = 0.34), 310.6 (f = 0.26), 356.4 (f = 0.23)
		^{1}H NMR		
hydroxyl H	−4.33			
H(N) upper		4.04		
H(N) lower		−4.24		
meso Hs	~9	8.7−8.9	8.88 - 8.91	~8.8
pyrrolic Hs	8.34	8.2−8.5	A: 7.7	A: ~7.7
			B, C: ~8.7	B, C: 6.4−6.7
		^{13}C NMR		
Cα	150.8	A: 161.9, 163.9	A: 172.2	A: 178.4[a]
		B: 155.1, 149.2	B: 162.8	B: 189.8,[b] 192.0[c]
		C: 144.0, 148.2	C: 162.9	C: 190.2,[b] 191.7[c]
Cβ	126.1	A: 129.5, 133.0	A: 127.3	A: 133.7
		B: 126.9, 124.2	B: 126.8	B:122.4,[b] 125.2[c]
		C: 124.0, 125.0	C: 126.7	C:122.6,[b] 124.1[c]
meso Cs	108.3	A−B: 113.0	A−B: 112.0	A−B: 133.9
		B−C: 98.0	B−C: 96.6	B−C: 154.6
		C−A: 108.1	C−A: 112.0	C−A: 134.0

[a] Unsubstituted ring, A. [b] Cα closer to pyrrolic ring. [c] Cα between O-substituted rings.

TABLE 3. Most Intense (f = Oscillator Strength) UV/Vis Absorption Bands (nm) and ^{1}H and ^{13}C NMR Chemical Shifts, Relative to TMS at the Same Theory Level, for Subporphyrins with *Meso* N Linkages

	NSPBOH	NSPHH	NSPOO	NSPSS
absorption bands	420.0 (f = 0.14), 418.2 (f = 0.13)	570.1 (f = 0.11), 305.1 (f = 0.10), 509.4 (f = 0.08)	288.0 (f = 0.30), 441.8 (f = 0.11), 534.6 (f = 0.10)	632.9 (f = 0.04), 616.1 (f = 0.05), 443.9 (f = 0.05)
		^{1}H NMR		
hydroxyl H	−3.18			
H(N) upper		6.67		
H(N) lower		−3.53		
meso Hs				
pyrrolic Hs	8.2	7.5- 7.7	A: 6.8, 7.0	A: 7.3
			B, C: ~8.3	B, C: 5.9−6.2
		^{13}C NMR		
Cα	166.5	A: 172.3, 179.9	A: 176.5, 185.4	A: 173.3[a]
		B: 169.3, 157.7	B: 171.3, 162.6	B: 213.3,[b] 179.6[c]
		C: 151.2, 123.6	C:158.1, 162.6	C: 213.3,[b] 179.6[c]
Cβ	131.4	A: 124.7, 138.1	A: 123.1, 134.5	A: 139.8
		B: 133.0, 121.1	B: 134.8, 126.5	B: 109.8,[b] 140.9[c]
		C: 123.6, 123.3	C: 130.2, 127.1	C: 109.8,[b] 140.9[c]

[a] Unsubstituted ring, A. [b] Cα closer to pyrrolic ring. [c] Cα between O-substituted rings.

with larger oscillator strengths and energies than the other molecules here reported. **CSPOO** presents a conical geometry and has a strong absorption band (f = 0.71) at about 305 nm and, particularly, **PSPOO** displays an almost planar geometry and a strong absorption band (f = 0.63) close to the visible region of the electromagnetic spectrum (λ = 353 nm).

The effect of geometry distortion provoked by different atoms on the central zone of the molecule discussed above is also clearly reflected on the NMR spectra. In effect, for the hydroxyboron subporphyrins ^{1}H NMR chemical shifts indicate the existence of two groups of H atoms (three in the case of systems with C connectors): the pyrrolic H (and *meso* H) at lower fields and the hydroxy H at higher fields. The strong geometric distortion produced by the repulsion between the inner Hs in the free base subporphyrins when using N and C connectors seems to separate the π-system on the downward slant ring from the rest of the molecule. Consequently, one of these H atoms presents a positive chemical shift whereas the other shows a negative one. The important reduction of the repulsion between the inner H atoms when using P connectors in **PSPHH** is clearly shown by the fact that these two atoms present quite similar small positive chemical shifts now. In general, in the heterosubporphyrins **CSPOO**, **CSPSS**, **NSPOO**, **NSPSS**, **PSPOO**, and **PSPSS**, a splitting in the chemical shifts takes place, the pyrrolic H atoms of the unsubstituted ring, A, presenting a different chemical shift from the rest. All these effects are appreciably smaller when the connector atom is P (see Tables 2−4 and Figure 1S of the Supporting Information). For the hydroxyboron subporphyrins the ^{13}C NMR chemical shifts correspond to two C groups (three in the case of systems with C

TABLE 4. Most Intense (*f* = Oscillator Strength) UV/Vis Absorption Bands (nm) and ^{1}H and ^{13}C NMR Chemical Shifts, Relative to TMS at the Same Theory Level, for Subporphyrins with *Meso* P Linkages

	PSPBOH	PSPHH	PSPOO	PSPSS
absorption bands	505.9 (f = 0.04), 370.0 (f = 0.52), 371.2 (f = 0.38), 370.3 (f = 0.15)	540.7 (f = 0.01), 397.8 (f = 0.29), 370.6 (f = 0.24), 369.9 (f = 0.23), 388.2 (f = 0.21)	550.1 (f = 0.01), 353.3 (f = 0.63), 356.3 (f = 0.62)	406.45 (f = 0.18), 506.2 (f = 0.08), 730.0 (f = 0.07)
^{1}H NMR				
hydroxyl H	−5.44			
H(N) upper		1.56		
H(N) lower		2.00		
meso Hs				
pyrrolic Hs	9.25	~ 9.2	A: 8.9 B, C: 9.6−9.7	A: 8.6 B, C: 8.2−8.3
^{13}C NMR				
Cα	170.2	A: 185.0 B: 172.8b, 164.1[c] C: 172.8b, 164.1[c]	A: 187.4[a] B:188.4,[b] 185.4[c] C:188.4,[b] 185.4[c]	A: 194.2 B: 200.3, 206.7 C: 206.7, 200.4
Cβ	134.5	A: 139.4 B: 131.0 C: 132.2	A: 140.3 B:138.3,[b] 134.1[c] C:138.3,[b] 134.1[c]	A: 141.2, 141.2 B: 130.5, 132.6 C: 132.6, 130.5

[a] Unsubstituted ring, A. [b] Cα closer to pyrrolic ring. [c] Cα between O-substituted rings.

TABLE 5. NICS Values Calculated at the Ring Critical Point of the Electron Density for Each Subporphyrin Component Ring and at the Center of Each Macrocycle

	A	B	C	center
CSPBOH	−10.005	−10.123	−10.118	−21.382
CSPHH	−5.153	−11.623	−12.438	−12.926
CSPOO	−2.405	−14.712	−14.714	−14.591
CSPSS	−3.673	−17.220	−17.243	−12.805
NSPBOH	−8.546	−8.791	−8.770	−20.961
NSPHH	−3.672	−10.190	−11.628	−12.577
NSPOO	−0.186	−12.317	−12.428	−13.686
NSPSS	3.602	−11.560	−11.417	−12.413
PSPBOH	−9.034	−8.934	−8.934	−16.369
PSPHH	−4.034	−10.745	−11.119	−10.586
PSPOO	1.122	−13.440	−13.440	−11.215
PSPSS	−0.512	−14.042	−14.055	−10.454

connectors): the α-carbon atoms, situated at lower fields, and the β ones at higher fields (in **CSPBOH** the *meso* C atoms appear at even larger fields). When passing to the free base subporphyrins and to the heterosubporphyrins the chemical shifts of these groups of carbon atoms appreciably split, although when the connector is P the two groups of signals corresponding to α- and β-carbon atoms are still clearly recognizable.

NICS values collected in Table 5 allow seeing the influence of *meso* linkages and heteroatom substitution in the inner shell on the aromaticity of these systems. For all the BOH subporphyrins the three pyrrolic rings are similar in every aspect, so their NICS values are also similar (around −10.0 for **CSPBOH**, −9.0 for **PSPBOH**, and −8.7 for **NSPBOH**). However, for free base subporphyrins and for diheterosubstituted ones, ring A shows a much smaller NICS in absolute value, whereas at rings B and C NICS values are larger than in the corresponding BOH system. Global aromaticity can be qualitatively measured by the NICS value at the center of each subporphyrin. The last column in Table 5 displays the most negative NICS values, that is, the larger aromaticity, for subporphyrins with C *meso* connectors, followed by those with N and P *meso* connectors. It has been pointed out earlier that P connectors tend to interrupt electron density delocalization, so it is not surprising to find now the smallest global aromaticity for these subporphyrins. For each connector family, the BOH compound seems to be the most aromatic, with the dioxygen substituted one in the second place of the aromaticity scale.

4. Conclusions

We have theoretically investigated the tolerance of heteroatom replacements in the pyrrole subunits (hydroxyboron complexes, free base subporphyrins, dioxygen, and dithio heterosubporphyrins), and the effect of using CH, N, and P as *meso* bridging connectors in subporphyrinoid systems. The geometrical structure of these systems is mainly determined by the internal area delimited by the *meso* atoms and the α-carbon atoms of the pyrrolic rings, and by the number and nature of the atoms located in this area. The hydroxyboron subporphyrins (**CSPBOH**, **NSPBOH**, and **PSPBOH**) display a conical shaped geometry, whose depth is smaller the larger the length of the *meso* connecting bonds. This conical shape is also present in dioxo (**CSPOO**) and dithio (**CSPSS**) subporphyrins with CH *meso* connectors. The presence of strong repulsions between the atoms on the central zone of the system (**CSPHH**, **NSPHH**, **PSPHH**, **NSPOO**, **NSPSS**, and **PSPSS**) provokes a correlative tilting of one of the three rings and loss of the conical shape with important consequences on spectroscopic properties. A particularly interesting case is **PSPOO** in which the large area of the central zone determined by the P connectors allows for an almost planar geometry that endows it with special features. The molecules presenting a tilted ring display weak absorption bands. Generally, the intensity of the bands moderatly increases when the geometry is cone shaped with the exception of **NSPBOH**, which presents the largest conical depth. Interestingly, **CSPOO**, which shows conical shape geometry, and **PSPOO**, which is almost planar, present strong absorption bands. ^{1}H and ^{13}C chemical shifts clearly reflect the effect of geometry distortion provoked by repulsion between the atoms on the central area of the system indicating a deep perturbation of the π system of the molecules. The global aromaticity of the subporphyrins with P connectors is smaller than that for systems with other connectors, as P partially beaks the electron density delocalization.

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Supporting Information Available: The Cartesian coordinates of all the optimized structures and a graphical representation of their absorption and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.