Theoretical Insight into Pyrrole Inversion and Planarity in 5,10,15,20-Tetraphenylsapphyrin and 5,10,15,20-Tetraphenyl-26,28-Diheterosapphyrins with Two O, S, or Se Atoms

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Density functional calculations at the B3LYP/6-31+G(d) (LACVP(D) for Se) theory level have been carried out on 5,10,15,20-tetraphenylsapphyrin (**TPS**), 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin (**TP2OS**), 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin (**TP2SS**), and 5,10,15,20-tetraphenyl-26,28-diselenasapphyrin (**TP2SeS**). In agreement with experimental findings, our theoretical results show that **TPS** and **TP2OS** present an inverted conformation, whereas **TP2SS** and **TP2SeS** are more stable in the normal one. It was found that the relative stability of the normal and inverted conformers of the just mentioned sapphyrins correlates positevily with their degree of planarity and aromaticity, which depends on the size of the heteroatom, the steric repulsions produced by phenyl rings at the meso C atoms, and the network and nature of the bond critical points (BCPs) inside the macrocycle. These BCPs have been characterized by means of the AIM analysis and, some selected ones, by the changes in the total energy of significant fragments when distorted to avoid them.

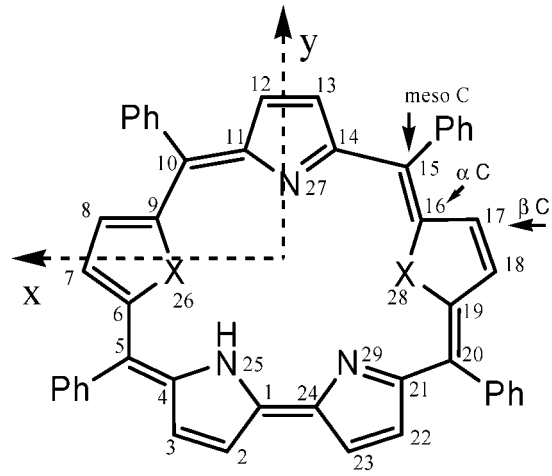
Introduction

Sapphyrins are the simplest expanded porphyrins and constitute a growing family of compounds, which have been the subject of many investigations in these years.[1−6] Their core contains an additional pyrrole ring giving rise to a bipyrrole subunit (see Scheme 1). Sapphyrins are important from basic and applied viewpoints, especially in coordination chemistry, as potential photosensitizing agents in the treatment of cancer diseases[7,8] and other practical applications.[9]

An interesting family of sapphyrins is that of heterosapphyrins in which some core NH groups belonging to a pyrrol have been replaced by other donor atoms such as O, S, and Se. The incorporation of these heteroatoms into the core of the macrocycle leads to an alteration of the cavity size and electronic structure, thus providing interesting spectroscopic, chemical, and physical properties, which can find applications in biology, medicine, material science, and catalysis.[10] 5,10,15,20-Tetraphenylheterosapphyrins have been synthesized in the past decade,[11−15] and several surprising facts concerning their conformation have been reported. ^{1}H NMR spectroscopic studies suggest that 5,10,15,20-tetraphenylsapphyrin and 5,10,15,20-tetraphenyldioxasapphyrin present the pyrrole ring opposite the bipyrrolic unit inverted (inverted conformation), whereas diheterosapphyrins with S and Se show the three N atoms toward the internal cavity (normal conformation).[11,13] On the other hand, DFT calculations on sapphyrin and dioxasapphyrin without meso substituents render the normal conformation as the most stable one.[16,17] It seems clear that the nature of the heteroatoms along with the presence of meso phenyl substituents are the factors affecting the conformation of the sapphyrins. The question is how do they influence it?

In order to answer the above question, we undertook a theoretical analysis of 5,10,15,20-tetraphenylsapphyrin, **TPS,** 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin, **TP2OS**, 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin, **TP2SS,** and 5,10,15,20-tetraphenyl-26,28-diselenasapphyrin, **TP2SeS**, focusing our attention on their electronic and molecular structure. In this work, the most stable tautomer of each sapphyrin is considered. **TPS** tautomer with H atoms bonded to N25, N27, and N28 is the selected one. For the heterosapphyrins, degenerate tautomers with internal H atom bound to N25 or N29 atoms are reported to be the most stable ones,[17] therefore, tautomer N25 will be studied.

SCHEME 1: Atom Numbering in Sapphyrins



X = NH, O, S, Se

Computational Methodology

Full geometry optimizations were performed by employing the DFT method based on Becke's three parameter hybrid functional and gradient-corrected correlation functional of Lee

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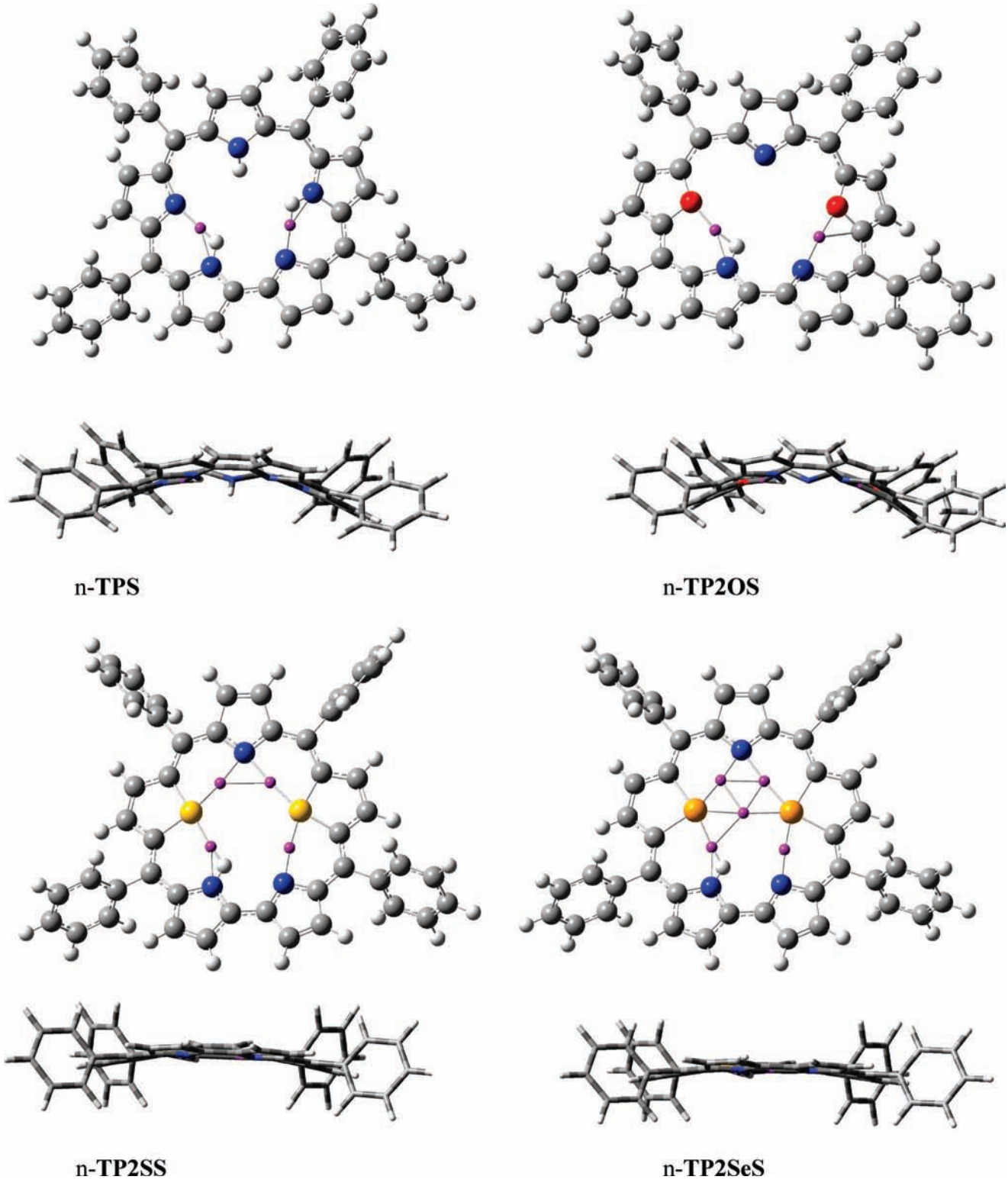


Figure 1. B3LYP/6-31+G(d) (LACVP(D) for Se) optimized structures of the tetraphenylsapphyrins studied in their normal conformation (top and side view). Purple balls are BPCs of the electronic density obtained with the AIM theory.

et al. (B3LYP),[18−20] by using the relativistic effective core pseudopotential LACVP(D) for Se[21] and the 6-31+G(d) basis set[22] for the remaining atoms as implemented in the JAGUAR program.[23] The characterization of the stationary points as minimum energy structures was further checked by computations of harmonic vibrational frequencies.

Nucleus-independent chemical shifts (NICS)[24] were calculated at the ring critical point at the center of the macrocycle of each investigated sapphyrin as an aromaticity index, by using the GIAO method as implemented in the Gaussian 03 program[25] at the former theory level (for heterosapphyrins with Se, NICS were evaluated at the bond critical point (BPC) located between both Se atoms). The electron density was also analyzed by means of the atoms in molecules theory, AIM,[26,27] of Bader, by using the AIMPAC package[28] for the sapphyrins in their ground states, that is, as singlets.

Computational schemes (B3LYP/6-31G(d,p)//3-21G, B3LYP/6-31G(d,p)//6-31G, B3LYP/6-31G(d), B3LYP/6-31G(d,p),

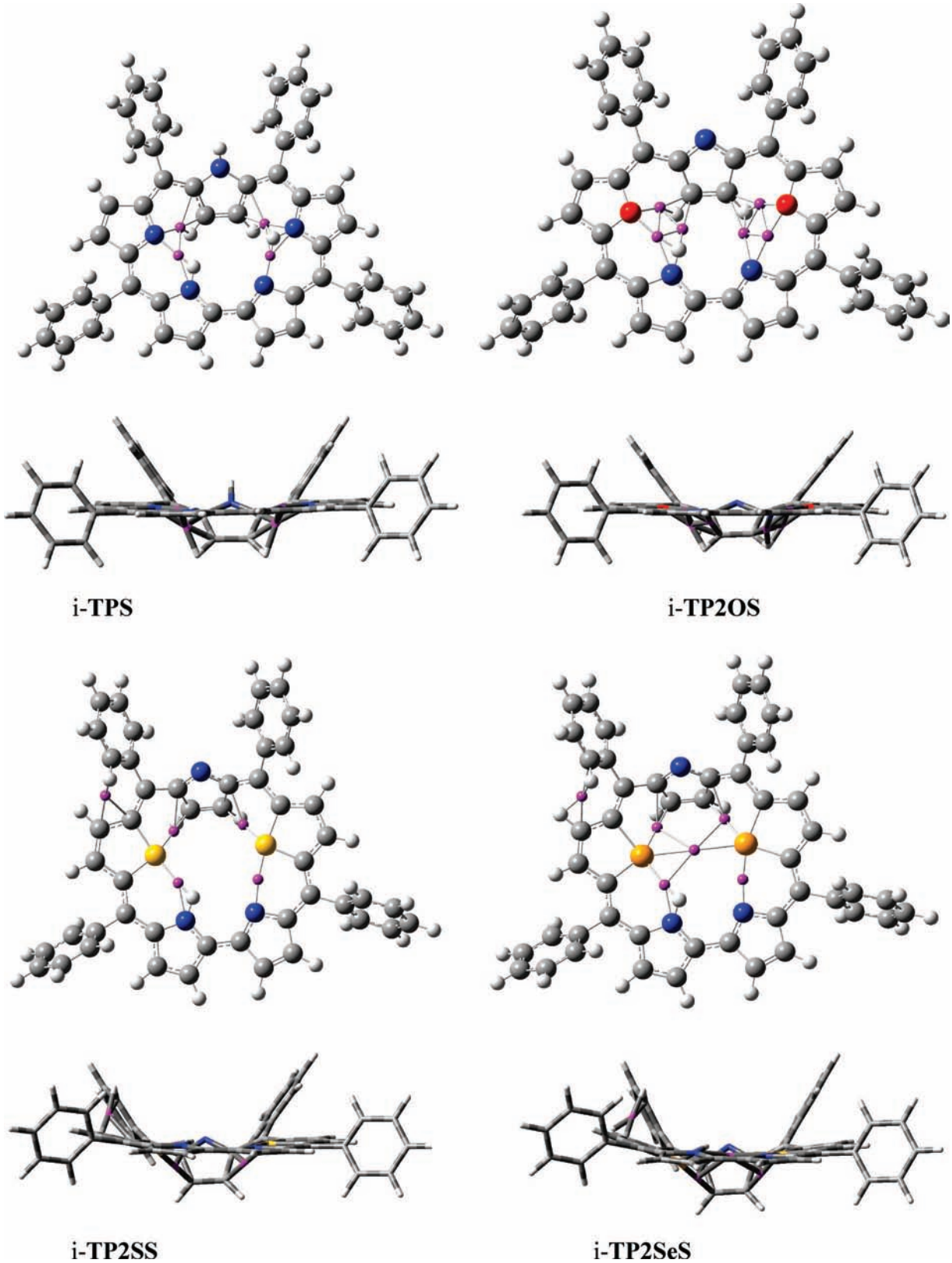


Figure 2. B3LYP/6-31+G(d) (LACVP(D) for Se) optimized structures of the tetraphenylsapphyrins studied in their inverted conformation (top and side view). Purple balls are BPCs of the electronic density obtained with the AIM theory.

B3LYP/6-31+G(d), B3LYP/6-311+G(d)) similar to those used in this work have demonstrated their applicability to the study of structure, energy, and electronic and magnetic properties of related macrocyclic compounds such as sapphyrins themselves,[13,16,29,30] heterosapphyrins,[17] carbaporphyrins,[31] heteroporphyrins,[32] and N-confused porphyrins.[33,34] Moreover, to check the accuracy of our theory level, we compared the X-ray diffraction experimental values available for two of the heterosapphyrins investigated in this work, 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin and 5,10,15,20-tetraphenyl-26,28-diselenasapphyrin,[14] to those found by us. The computed bond lengths involved in the inner macrocycle differed from the

TABLE 1: B3LYP/6-31+G(d) (LACVP(D) for Se) Electronic Energies (in Atomic Units) of the Studied Sapphyrins in their Ground State[a]

sapphyrins	normal	inverted
TPS	−2122.77260 (470.7)	−2122.78271 (470.9)
TP2OS	−2162.45451 (453.4)	−2162.47298 (454.4)
TP2SS	−2808.42518 (449.9)	−2808.40456 (448.4)
TP2SeS	−2030.43987 (447.5)	−2030.40848 (446.1)
S	−1198.55964 (252.5)	−1198.53889 (249.9)
2OS	−1238.24211 (233.5)	−1238.23705 (232.3)

[a] Zero-point energies (in kcal/mol) are shown in parenthesis.

experimental values by −0.003 to +0.023 Å for 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin and by −0.014 to +0.038 Å for 5,10,15,20-tetraphenyl-26,28-diselenasapphyrin. The bond angles differed from the experimental ones by −1.2 to +1.0°. For both heterosapphyrins, the distances and bond angles wherein the S and Se atoms are involved present the largest deviations. The planarity of these two calculated macrocycles is similar to that experimentally found. The computed C9−C10−C11−C12 dihedral angle presented a deviation of −4.1° for 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin and −1.8° for 5,10,15,20-tetraphenyl-26,28-diselenasapphyrin. These relatively small deviations confirm the validity of our computational method.

Results and Discussion

Figures 1 and 2 collect the optimized structures for the normal and inverted forms of the sapphyrins investigated in this work, respectively, and Table 1 shows their corresponding energies.

Contrary to the other normal heterosapphyrins (named by writing n- before their symbolic name), n-**TPS** and n-**TP2OS**, are not planar but present a saddle conformation (see Figure 1). The four meso C atoms along with both X26 and X28 atoms (X = N, O) and N27 are nearly in the same plane, say *XY* reference plane, with positive values of *X* and *Y* coordinates toward X26 and N27, respectively, (see Scheme 1), and positive *Z* values down this plane (*Z* coordinates of meso C atoms, X26, X28, and N27 atoms are lower than ± 0.1Å). Bipyrrolic N atoms, N25 and N29, are about 0.5 Å above the reference plane, and β C atoms of the pyrrole and bipyrrolic subunits between 0.8 and 1.2 Å are also above it, wheres β C atoms of the two remaining rings are about 1 Å under the reference plane. The macrocycles in n-**TP2SS** and n-**TP2SeS** are essentially planar. The four inverted heterosapphyrins present a similar shape (see Figure 2): both heterocyclopentenes and the bipyrrolic unit lay almost in the same plane, and the inverted pyrrole ring is tilted with C9−C10−C11−C12 dihedral angles of 23.9°, 24.3°, 39.2°, and 40.6° for i-**TPS**, i-**TP2OS**, i-**TP2SS**, and i-**TP2SeS**, respectively. Another significant geometry difference between normal and inverted sapphyrins concerns the angles, the vertices of which are meso C atoms (see Supporting Information). In normal sapphyrins, those flanking the upper pyrrole ring, α_{10} and α_{15}, are larger than those flanking the bipyrrolic unit, α_5 and α_{20}, mainly in n-**TPS** and n-**TP2OS**. However, α_{10} and α_{15} in inverted sapphyrins are clearly smaller than α_5 and α_{20} in all of the sapphyrins. On the other hand, the phenyl substituents at the meso C atoms are not perpendicular to the reference plane neither in the normal nor in the inverted conformations. Those near the bipyrrole unit present their bottom part toward this unit, as it happens for those near the pyrrole ring opposite. Thus, both N, O, S, or Se heterocycles are partially covered in their upper face by the top part of the phenyl rings. Only in i-**TP2SS** and i-**TP2SeS**, the phenyl ring bonded to C5 breaks this disposition.

Our energy calculations (collected in Table 1) show that i-**TPS** and i-**TP2OS** are 6.1 and 10.6 kcal/mol, respectively, more stable than their normal conformers, but for S and Se sapphyrins, normal isomers are more stable than inverted ones by 11.4 and 18.3 kcal/mol, respectively, by taking into account zero-point energies. This is in agreement with experimental ^{1}H NMR[11,13] and X-ray data.[14] It is also interesting to note that the greater the heteroatom, the largest the energy difference between both conformations.

At this point, two striking questions arise. Why are n-**TPS** and n-**TP2OS** not more stable than their inverted conformations as it happens to the S and Se heterosapphyrins? Why are n-**TPS** and n-**TP2OS** not planar as the remaining normal heterosapphyrins?

It is known that planarity reinforces aromaticity in aromatic molecules. Neither the normal nor the inverted conformations of **TPS** and **TP2OS** are planar; therefore, we shall take NICS values at the ring critical point at the center of these sapphyrins as an indicative of their aromaticity. For n-**TPS** and n-**TP2OS**, NICS values are −12.55 and −12.03, respectively, and for i-**TPS** and i-**TP2OS**, they are −13.07 and −13.35, respectively; therefore, the most stable conformations, the inverted ones, present the largest aromatic character. NICS values for n-**TP2SS** and n-**TP2SeS** are −12.95 and −14.58, respectively, and for i-**TP2SS** and i-**TP2SeS**, they are −11.30 and −11.99, respectively, clearly indicating that the most stable conformations, now the normal ones, show the largest aromatic character again. Therefore, a positive correlation between aromaticity and stability is found for the sapphyrins investigated in this work. Although some theoretical studies on a variety of N-confused porphyrins have revealed that the predominance of the steric repulsion in the core over the aromaticity can change the positive correlation aromaticity−stability,[33,34] this seems not to happen in our case.

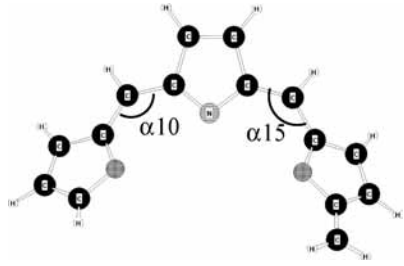
The approximately planar molecular structures can be considered the key of conformation stability; therefore, the question about n-**TPS** and n-**TP2OS** non-planarity becomes essential. The nature of the heteroatoms may affect the attractive interactions inside the macrocycle. The AIM theory analyses the topology of the electronic density and identifies the BCPs among all of the atoms in a chemical species; therefore, we apply this theory to the eight sapphyrins under study, and we actually find different interaction patterns. Figures 1 and 2 also show the BCPs of the electronic density located in the internal core of the studied sapphyrins, and Table 2 shows the corresponding values of their electron density. n-**TPS** and n-**TP2OS** present only two BCPs inside the macrocycle, one between N25 and X26 (X = N, O) and the other between X28 and N29. In i-**TPS** and i-**TP2OS**, the two last-described BCPs are reinforced (they present larger electronic density at the BPC), and besides, two new ones appear, involving C12 and C13 atoms (see Table 2). Furthermore, in the case of i-**TP2OS**, there are another two weak BCPs between the β C atoms of the inverted pyrrol and the N atoms of the bipyrrolic unit. n-**TP2SS** shows the same two interactions as those present in n-**TPS** and n-**TP2OS** and two new ones involving both S26 and S28 atoms and the N27 atom. The larger size of S atoms compared to that of the N and O ones makes the bonds to N27 possible. In the i-**TP2SS**, the BCPs involving S26, S28, and the bipyrrolic N atoms are reinforced, whereas those affecting N27 are replaced by two bonds between S atoms and C12 and C13. Besides, a weak BCP between the phenyl ring bonded to C10 and C8 appears. The network of

TABLE 2: Electronic Density, ρ, (in Atomic Units) at the BPCs Located Inside the Macrocycle of the Studied Sapphyrins through the AIM Theory

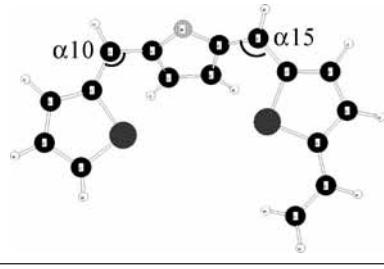
n-**TPS**	ρ	n-**TP2OS**	ρ	n-**TP2SS**	ρ	n-**TP2SeS**	ρ
N26−N25	0.0178	O26−N25	0.0099	S26−N25	0.0132	Se26−N25	0.0135
N28−N29	0.0192	O28−N29	0.0094	S28−N29	0.0135	Se28−N29	0.0149
				S26−N27	0.0096	Se26−N27	0.0128
				S28−N27	0.0077	Se28−N27	0.0091
						Se26−Se28	0.0052
i-**TPS**	ρ	i-**TP2OS**	ρ	i-**TP2SS**	ρ	i-**TP2SeS**	ρ
N26−N25	0.0201	O26−N25	0.0111	S26−N25	0.0156	Se26−N25	0.0144
N28−N29	0.0226	O28−N29	0.0099	S28−N29	0.0172	Se28−N29	0.0192
N26−C12	0.0139	O26−C12	0.0144	S26−C12	0.0161	Se26−C12	0.0165
N28−C13	0.0120	O28−C13	0.0151	S28−C13	0.0140	Se28−C13	0.0132
		C12−N25	0.0058	Phe10−C8	0.0085	Phe10−C8	0.0086
		C13−N29	0.0044			Se26−Se28	0.0030

n-**S**	ρ	n-**2OS**	ρ
N26−N25	0.0127	O26−N25	0.0077
N28−N29	0.0185	O28−N29	0.0070
N26−N27	0.0061		
i-**S**	ρ	i-**2OS**	ρ
N26−N25	0.0170	O26−N25	0.0093
N28−N29	0.0196	O28−N29	0.0087
N26−C12	0.0143	O26−C12	0.0145
N28−C13	0.0123	O28−C13	0.0153
		C12−N25	0.0047
		C13−N29	0.0038

TABLE 3: B3LYP/6-31+G(d) Geometry and Energy of Fixed and Distorted Fragments of n-TP2OS, n-TP2SS, i-TP2OS, and i-TP2SS



	N-Fixed			N-Distorted		
	α10	α15	*E* (au)	α10	α15	*E* (au)
TP2OS	130.8	130.5	−783.27199			
TP2SS	127.6	129.1	−1429.27313	136.0	136.0	−1429.26686



	I-Fixed			I-Distorted		
	α10	α15	E(au)	α10	α15	E (au)
TP2OS	119.6	119.4	−783.29143	130.0	133.0	−783.29227
TP2SS	117.5	118.0	−1429.21827	131.0	125.0	−1429.22448

BCPs inside the core of normal and inverted **TP2SeS** is analogous to that described for **TP2SS** except that, because Se atoms are larger than S ones, a weak BCP between both Se atoms emerges. The above data indicate that the i-**TPS** and i-**TP2OS** present more interactions than their corresponding normal conformers, but in i-**TP2SS** and i-**TP2SeS**, interactions between X (X = S, Se) and N27 of the normal sapphyrins are replaced by other ones involving atoms quite separated from the plane containing the rest of the macrocycle. The interactions affecting phenyl ring bonded to C10 at i-**TP2SS** and i-**TP2SeS** cannot compensate the loss of stabilization of these inverted sapphyrins.

The existence of a BCP implies the concentration of certain electronic density in the region among atoms, but it does not ensure an energy stabilization of the system, as this depends on several factors.[35−39] The main differences among the internal nets of BCPs found in the sapphyrins under study affect the X26−N27 and X28−N27 interactions for the normal conformations and the X26−C12 and X28−C13 ones for the inverted conformations (X = N, O, S, Se). When looking for a relationship between the relative stability of the molecules and the presence of BCPs, we calculated the energy of fragments N and I (see Table 3) for **TP2OS** and **TP2SS** (without the two phenyl rings at meso carbon atoms for the sake of simplicity), each one in two ways: one with the fixed geometry they present at the corresponding heterosapphyrin, and the other with a geometry distorted by enlarging the meso angles α_{10} and α_{15} to a value for which the BCP is not present (distorted N-**TP2OS** was not calculated as the fixed fragment lacks of the O26−N27 and O28−N27 BCPs). These selected sapphyrin fragments represent the two different conformational behaviors found, and the geometry distortion just described does not alter the planarity of the fragments. The obtained results are collected in Table 3.

The comparison of the energy of N-**TP2SS** fragments fixed and distorted indicates that the absence of S26−N27 and S28−N27 BCPs destabilizes the system; therefore, this interaction can be considered stabilizing. On the contrary, the comparison of the energy of both I-**TP2OS** fixed and distorted as well as I-**TP2SS** fixed and distorted shows that the interactions X26−C12 and X28−C13 (X = O, S) could

be considered destabilizing, because their presence makes the molecular structure more unstable, in the same way as in the planar transition state for biphenyl rotation.[36] The fixed fragments considered in these calculations present the same energy ordering as that of the heterosapphyrins they belong to (I-**TP2OS** fixed fragment is more stable than N-**TP2OS**, with the reverse energy ordering for **TP2SS** fragments). This suggests that the main reasons for the pyrrol inversion or not inversion are already present in the fragments considered, and they are somewhat related to the presence and nature of the BCPs. When generalizing our results to the four studied sapphyrins, a factor for n-**TPS** and n-**TP2OS** destabilization is the absence of X26−N27 and X28−N27 BCPs, whereas n-**TP2SS** and n-**TP2SeS** are stabilized by the presence of these BCPs (this fact has significant implications in planarity and aromaticity, as we shall discuss later). On the other hand, all of the inverted conformations show destabilizing X26−C12 and X28−C13 BCPs to be unavoidable because of the geometrical constraints imposed by the macrocycle structure and to the orbital overlap necessary to favor electronic delocalization. For i-**TPS** and i-**TP2OS**, these destabilizations are compensated by factors such as an aromaticity greater than that in their normal conformations; therefore, they become more stable. For i-**TP2SS** and i-**TP2SeS**, the destabilizing effect of X26−C12 and X28−C13 BCPs adds to the loss of aromaticity to yield the inverted conformations less stable than the normal ones.

As we have just shown, n-**TPS** and n-**TP2OS** are the only sapphyrins that do not present stabilizing interactions between X26 and X28 (X = N, O) and N27. Therefore, the lack of stress in their internal core provides these molecules with a large flexibility, and they can easily leave the planarity. However, the more planar the macrocycle, the greater the π conjugation, the aromaticity, and the stability. The only reason for these molecules to bend is that phenyl substituents at meso carbon atoms force them to bend in order to minimize steric repulsions. To test this hypothesis, we analyzed sapphyrin, **S**, and 26,28-dioxasapphyrin, **2OS** (without phenyl substituents), at the same theory level than that for the meso-substituted sapphyrins, and we obtain n-**S** and n-**2OS** planar and more stable than the inverted ones by 13.05 and 3.20 kcal/mol, respectively, in agreement with previously reported data[16,17] (see Table 1). As can be seen in Table 2, the AIM analysis of both conformations of **S** and **2OS** shows the same interactions inside the macrocycle as that in the corresponding tetraphenylsapphyrins (only a new weak N26−N27 bond appears in n-**S**), but now, phenyl groups are not present; therefore, there are no steric repulsions forcing the macrocycle to bend.

Conclusions

Our study indicates that the non-planarity in n-**TPS** and n-**TP2OS** is due to the steric repulsions among phenyl rings and β carbon atoms of their neighbor cycles along with the fact that N and O atoms are not big enough to interact to N27, thus rendering a large flexibility of the macrocycle. Their inverted isomers, i-**TPS** and i-**TP2OS**, although not completely planar because of the inverted pyrrole and presenting unstabilizing BCPs between X26−C12 and X28−C13, are more aromatic and more stable. Heterosapphyrins with S and Se atoms in their normal conformation present a network of interactions in the internal cavity, which contribute to their planarity, their larger aromaticity, and their greater stability.

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Supporting Information Available: Cartesian coordinates of the studied sapphyrins and some relevant geometry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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