Geometry and Tautomerism of 26,28-Dioxasapphyrin and 26,28-Dithiasapphyrin: DFT Studies

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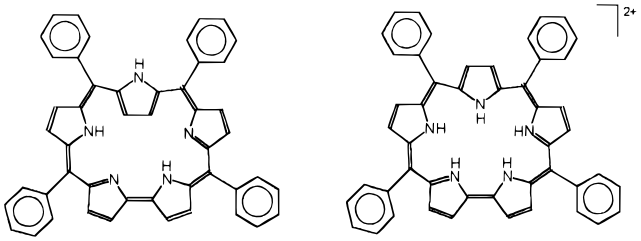
The density functional theory (DFT) calculations have been carried out on 26,28-dioxasapphyrin (O_2SapH) and 26,28-dithiasapphyrin (S_2SapH) including all likely geometrical isomers and NH tautomers. The peculiar skeleton of sapphyrin with an inverted pyrrole ring lying opposite to the bipyrrolic unit (**I**) and the regular planar arrangement (**P**) of the macrocycle with three nitrogens and two heteroatoms pointing to the center of the macrocycle were considered. Consequently, a total of eight structures resulting from the feasible geometrical isomerism and NH tautomerism of diheterosapphyrins were studied. The optimized bond distances and angles of 26,28-diheterosapphyrins compare favorably with the relevant X-ray structures of sapphyrins and heterosapphyrin. The pyrrole bond distances decrease in the series: $C_\alpha-C_\beta > C_\alpha-C_{meso} > C_\alpha-N > C_\beta-C_\beta$, reproducing the pattern of the regular porphyrin or dicationic sapphyrins. There is an appreciable effect from the aromatic character of the macrocycle on the furan or thiophene moieties. These $C_\alpha-C_\beta$ distancs are longer and the $C_\beta-C_\beta$ distances are shorter than those in free furan or thiophene. The relative stability of the postulated tautomeric forms decreases in the order of {25-NH, 27-N, 29-N} **P***25* > {25-NH, 27-N, 29-N} **I***25* > {25-N, 27-NH, 29-N} **P***27* > {25-N, 27-NH, 29-N} **I***27* for O_2SapH and {25-NH, 27-N, 29-N} **P***25* > {25-N, 27-NH, 29-N **P***27* ≫ {25-NH, 27-N, 29-N} **I***25* > {25-N, 27-NH, 29-N} **I***27* for S_2SapH. The formation of the inverted 26,28-dithiasapphyrin structure is strongly energetically disfavored (ca. 30 kcal/mol). Both extreme geometries **P** and **I** are energetically accessible for 26,28-dioxasapphyrin. The localization of the NH proton on the bipyrrolic fragment is evidently preferred in each investigated case.

Introduction

Core modification of 5,10,15,20-tetraphenylsapphyrin by an introduction of various heteroatoms in place of nitrogen atoms permits the preparation of a series of new expanded porphyrins that may have interesting properties in terms of their aromatic properties and ability to bind metal ions.[1,2] Perspectively, they can be used as potent anion chelating reagents and particularly as likely photosensitizers in the photodynamic therapy. The series of heteroatom-containing sapphyrins constitutes a group in which the extent and localization of substitution can be systematically varied. For instance, considering the monoheterosubstituted skeleton, three isomers can be constructed: 25-, 26-, 27-heterosubstituted sapphyrins. The hypothetical disubstitution creates six isomers, specifically 25,29-; 25,26-; 25,-27-; 25,28-; 26,27-; and 26,28-diheterosubstitued sapphyrin. The following pyrrole-alkylated expanded porphyrin derivatives with one or two pyrrolic fragments replaced by furan were investigated: 27-oxasapphyrin,[3,4] 25,29-dioxasapphyrin,[3] dioxasmaragdyrin,[3] ozaphyrin (isomeric analogue of oxasapphyrin),[5] oxobronzaphyrin (isomeric analogue of rubyrin),[6] and tetraoxarubyrin.[7] The expanded porphyrins containing thiophene(s) instead of pyrrole(s) were also synthesized: 27-thiasapphyrin,[3,4] 25,29-dioxa-27-thiasapphyrin,[4a] oxobronzaphyrin,[6] bronzaphyrin,[8] and thioozaphyrin (isomeric analogues of thiophen-containing sapphyrins),[8] decaethylpentathiaphyrin dication related to pentaphyrin,[9] hexathiahomoporphycene dication with the bronzaphyrin-like skeleton,[10] and tetrathiarubyrin.[7]

By analogy to core-modified 5,10,15,20-tetraarylporphyrins,[11−15] we have recently enlarged the class of 5,10,15,-20-tetraphenylsapphyrin by an addition of two core-modified 5,10,15,20-tetraphenylsapphyrins.[16,17] Formally they are formed by a replacement of 26-N and 28-N nitrogen atoms by oxygen or sulfur, respectively, yielding 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin (O_2TPSH) and 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin (S_2TPSH).[18] Recently, the X-ray crystal structure of S_2TPSH has been reported.[19]

SCHEME 1



The unusual flexibility of the macrocyclic skeleton was determined for the prototype 5,10,15,20-tetraphenylsapphyrin ($TPSH_3$) molecule.[16,17] Two fundamental structures, inverted and planar, were detected in the case of $TPSH_3$ and its dication $TPSH_5^{2+}$ as shown in Scheme 1.

The reversible transformation of the macrocycle involves a reversible flip of a single pyrrole unit. In light of these peculiar dynamic properties of $TPSH_3$ an impact of the replacement of nitrogens by heteroatoms on the macrocycle structure has been a matter of a particular interest.[18] 5,10,15,20-Tetraphenyl-26,-28-dioxasapphyrin, which shows an inverted skeleton in each protonation stage (Scheme 2), contains only one exchangeable NH proton, and the tautomeric process involves its relocalization

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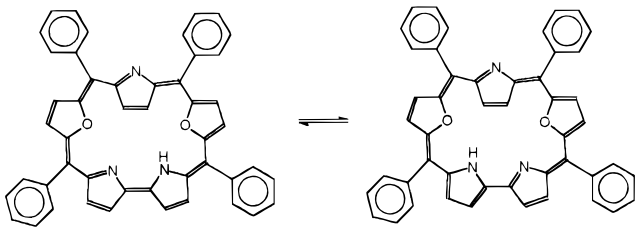
SCHEME 2



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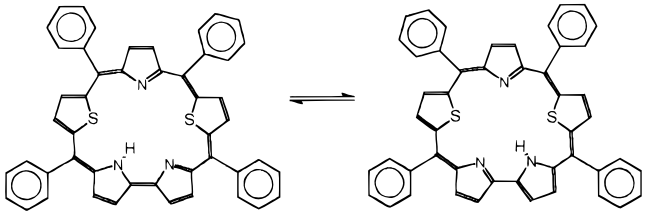


between two degenerate asymmetric structures.[18] The tautomeric equilibrium of 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin (S_2-TPSH), which shows the planar arrangement of the macrocycle (Scheme 3), includes also the exchange of proton between 25-N and 29-N. The process was found to be slow on the ^{1}H NMR time scale below 213 K.[18]

The density function theory methods and the high-level of ab initio calculations have been recently applied to porphyrins, porphyrin isomers, metalloporphyrins, and related systems.[20−26] The theoretical investigations addressed problems of geometry, NH tautomerisation, electronic spectra, and substituent effect on the electronic structure.

The spectacular flexibility of the sapphyrin (heterosapphyrin) skeleton raises the question of the relative stability of the invoked geometrical isomers and NH tautomers of 26,28-diheterosapphyrins. Thus, to approach this problem, we have performed theoretical investigations applying the density functional theory (DFT).

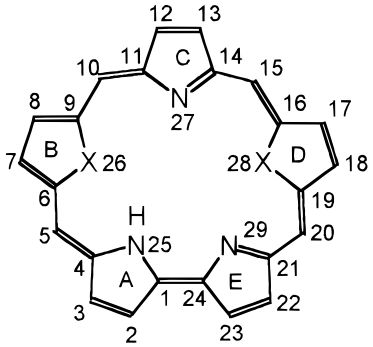
Method

Calculation Methods. The calculations were carried out with the GAUSSIAN94 program.[27] All structures were optimized within unconstrained C_1 symmetry of the system using the density functional theory (DFT) with Becke's three-parameter exchange functionals and the gradient-corrected functionals of Lee, Yang, and Parr (DFT(B3LYP)).[28] The final estimations of the total energies were performed at the B3LYP level with the 6-31G** basis set using the B3LYP/6-31G fully optimized structures. In a single case of the symmetric S_2SapH **P***27* tautomer, the structure was optimized using the 6-31G* basis set.

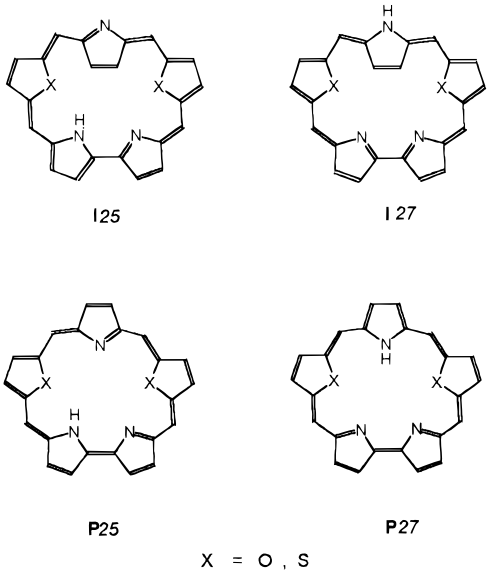
Results and Discussion

For simplification, all calculations have been carried out for plain 26,28-dioxasapphyrin (O_2SapH) and 26,28-dithiasapphyrin (S_2SapH). Therefore, the corresponding phenyl groups of 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin and 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin presented at Schemes 2 and 3 have been replaced by hydrogen. The general numbering pattern is presented in Scheme 4. The density functional theory calculations have been carried out for the neutral 26,28-diheterosapphyrin in two alternative planar and inverted geometries including all feasible NH tautomers as presented in Scheme 5. To simplify the description, we will refer further on

SCHEME 4



SCHEME 5



to the particular tautomeric species defining their idealized structure, i.e., **I***n* and **P***n* for the inverted and approximately planar geometries, respectively. The tautomers are consistently labeled by the number corresponding to the assignment of the protonated pyrrolic nitrogen. In general terms, three inverted tautomeric forms **I***25*, **I***27*, **I***29* and three planar **P***25*, **P***27*, **P***29* could be suggested for diheterosapphyrin (Scheme 5). As asymmetric tautomers **I***25* and **I***29* or **P***25* and **P***29* are pairwise degenerated; the calculations have been carried out for discernible **I***25*, **I***27* and **P***25*, **P***27* species.

The optimized structural parameters and calculated total energies are presented in Tables 1−5 and Figures 1−4, respectively. For the sake of comparison, the selected X-ray structural data of relevant sapphyrins and heterosapphyrins are included in Tables 1−3 as well.[29]

A general comparison of bond distances within the pyrrole and furan or thiophene fragments demonstrates that the extensive π delocalization exists through the macrocycle and extends to the heterocyclic fragment (Figures 1−4; Table 1). The bond distances of the regular pyrroles ($C_\alpha-C_\beta > C_\alpha-C_{meso} > C_\alpha-N > C_\beta-C_\beta$) reproduce the pattern of the regular porphyrin or dicationic sapphyrins.[29,30] All bond length and angles are in limits expected for porphyrins, heteroporphyrins, or sapphyrin.[4−6,16−19,29,30] There is an appreciable effect from the aromatic character of the macrocycle on the furan or thiophene moieties. In these macrocycles, the $C_\alpha-C_\beta$ distances are longer and the $C_\beta-C_\beta$ distances are shorter than in free furan[31a] or thiophene.[31b,c] The pattern of $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ distances follows that seen in the pyrrole rings. These bond changes

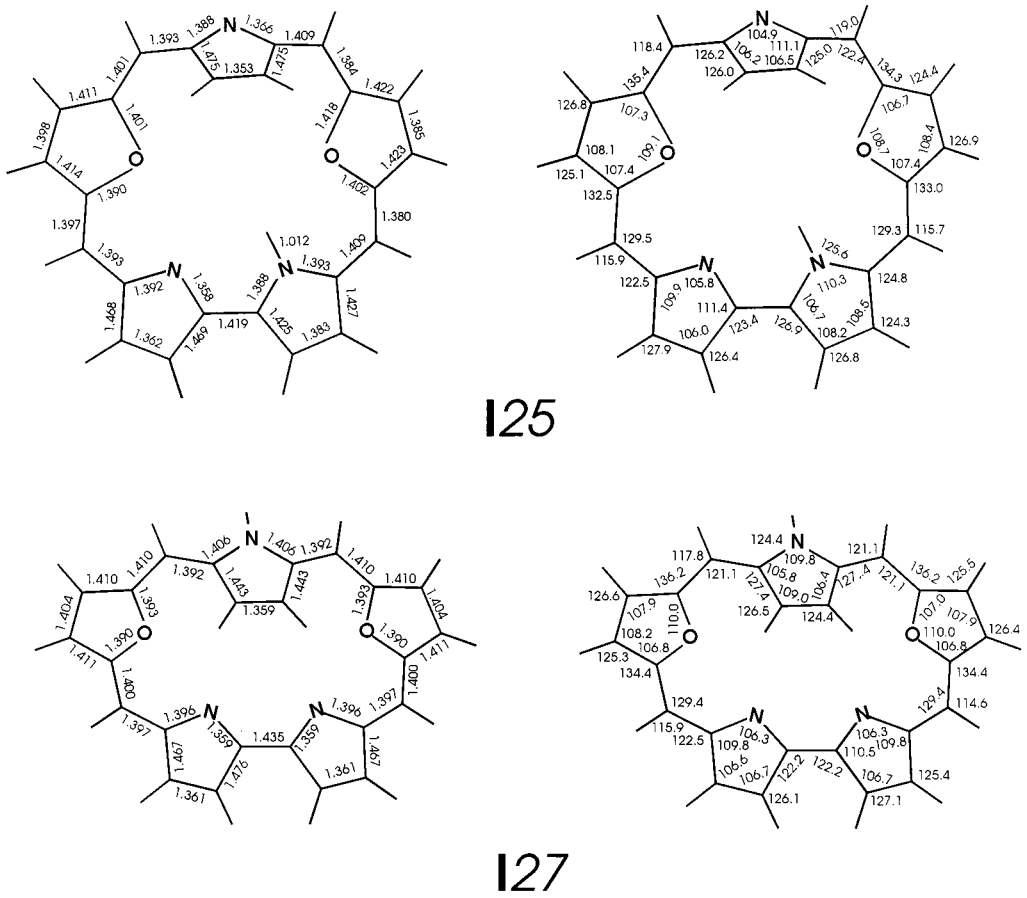


Figure 1. Calculated B3LYP/6-31G geometries of 26,28-dioxasapphyrin **I***25* and 26,28-dioxasapphyrin **I***27*. Bond lengths are in angstroms and the bond angles are in degrees.

TABLE 1: Representative Bond Distances of Heterocyclopentadiene Fragments in Heteroporphyrins (in Å)

compound	X−C_α	C_α−C_β	C_β−C_β	ref
O_2SapH **P***25*	1.410	1.424	1.377	*a*
O_2SapH **I***25*	1.390	1.414	1.398	*a*
ODTDPH[b]	1.380(4)	1.403(4)	1.363(4)	18
OSapCo$(CH_3COO)_2$[c]	1.390(6)	1.396(8)	1.355(7)	4c
furan	1.370	1.322	1.425	29a
S_2SapH **P***25*	1.838	1.423	1.377	*a*
S_2SapH **I***25*	1.808	1.411	1.396	*a*
S_2SapH **P***27*	1.831	1.415	1.384	*a*
S_2SapH **P***27*	1.766	1.416	1.379	*d*
S_2TPSH	1.755(3)	1.412(5)	1.359	19
S_2TPP[e]	1.748(4)	1.408(6)	1.367(7)	13
SSapRh$_2$(CO)$_4$[f]	1.727(13)	1.418(4)	1.354(6)	4c
thiophene	1.714(2)	1.370(3)	1.423(3)	29[b,c]

[a] This work, DFT optimized in the 6-31G basis set. [b] ODTDPH, 5,20-ditolyl-10,15-bisphenyl-21-oxaporphyrin. [c] OSapH$_2$, 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-oxasapphyrin. [d] This work, DFT optimized in the 6-31G* basis set. [e] S_2TPP, 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin. [f] SSapH$_2$ 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin.

indicate that the π delocalization through the furan or thiophene rings is altered in diheterosapphyrins. Altogether, these modifications suggest that the π electron density has been altered within the furan or thiophene fragments so that it is increased in the C_β−C_β bond and decreased in the C_α−C_β bond. The similar influence of the aromatic macrocycle on the delocalization pattern in the modified ring was experimentally determined in the case of tetraoxa[18]porphyrin(1.1.1.1) dication,[32] ozaphyrin,[5] thia-, oxa-, dioxa- and dithiaporphyrins,[12−14] oxa- and thiasapphyrins.[4,19]

TABLE 2: Selected Bond Angles for the DFT Optimized Structures[a]

	angles (deg)		
species	C(8)C(9)C(10)	C(9)C(10)C(11)	C(10)C(11)C(12)
O_2SapH **I***25*	135.4	118.4	126.2
O_2SapH **P***25*	125.2	137.2	118.5
O_2SapH **I***27*	136.2	121.1	127.4
O_2SapH **P***27*	126.9	136.9	120.3
S_2SapH **I***25*	130.7	121.9	125.5
S_2SapH **P***25*	125.4	129.3	123.3
S_2SapH **I***27*	130.0	119.8	126.9
S_2SapH **P***27*	124.9	131.3	125.1
S_2SapH **P***27*[b]	123.9	131.6	125.0
SapH^{2+} [c]	123.5	135.2	123.5
S_2TPSH[d]	123.8	129.6	121.0

[a] DFT optimized in the 6-31G basis set unless marked differently. [b] DFT optimized in the 6-31G* basis set. [c] Dication of 2,7,18,23-tetramethyl-3,8,12,13,17,22-hexaethylsapphyrin, from ref 27. [d] From ref 19.

The calculated C_α−O bond lengths remain practically unaltered as compared to furan. Contrary, the C_α−S bond lengths are systematically elongated in comparison to thiophene (0.10 Å) or thiaporphyrins (0.06 Å) (Table 1). This elongation has been related to the fact that the 6-31G basis set has been used for the geometry optimization. We have found that the application of the 6-31G* basis set resulted in the better reproduction of the C_α −S bond lengths which are equal to 1.766 Å. However, all other structural parameters remained practically invariable (Tables 1−3). Consequently, considering the size and number of analyzed structures we have compromised between quality of calculations and their affordability. Thus, we have restrictred ourselves to a 6-31G basis in investigation of the

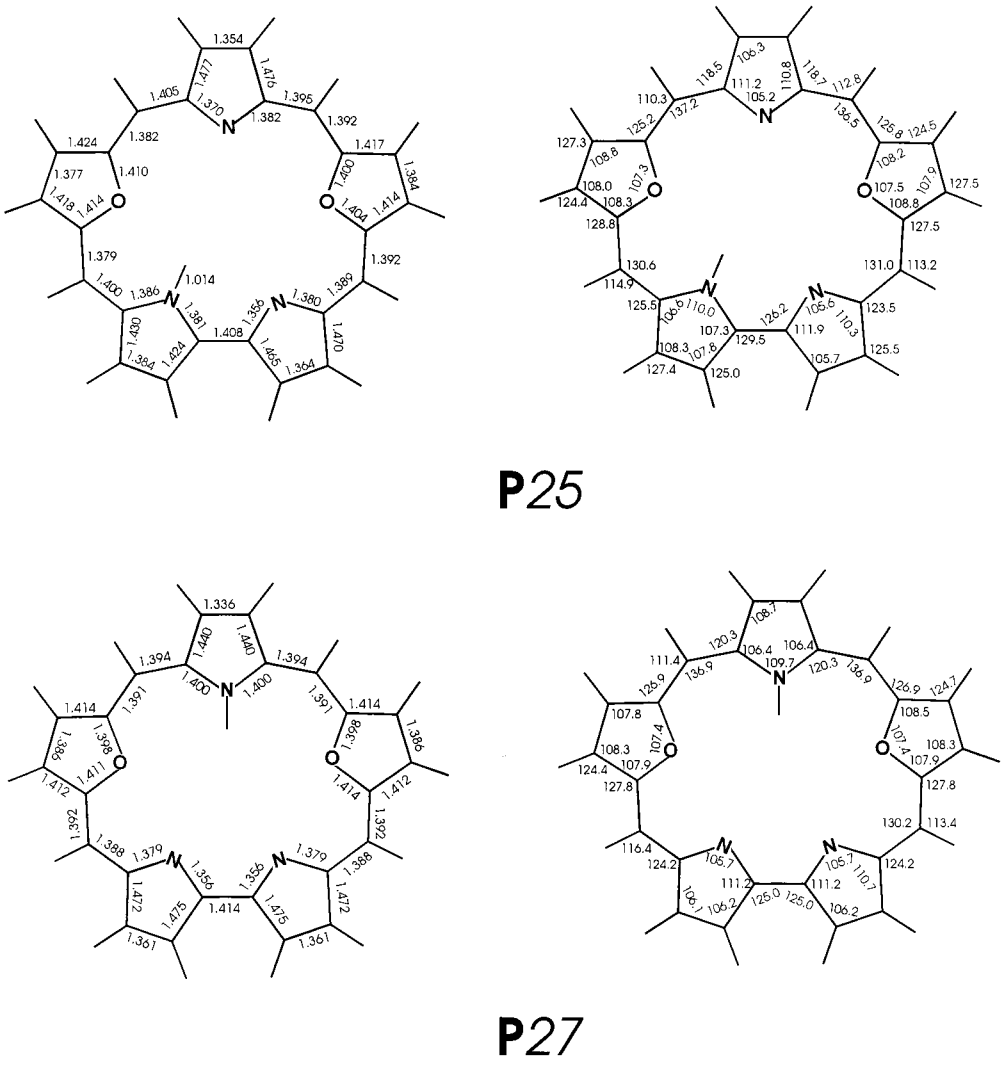


Figure 2. Calculated B3LYP/6-31G geometries of 26,28-dioxasapphyrin **P***25* and 26,28-dioxasapphyrin **P***27*. Bond lengths are in angstroms and the bond angles are in degrees.

TABLE 3: DFT Calculated Distances of the 26,28-Diheterosapphyrin Core[a]

	distance (Å)		
species	N(25)···N(29)	N(25)···X(26)	X(26)···X(28)
O_2SapH **I***25*	3.022	2.946	6.011
O_2SapH **P***25*	2.880	3.049	5.598
O_2SapH **I***27*	3.079	2.911	6.196
O_2SapH **P***27*	2.921	2.991	5.674
S_2SapH **I***25*	2.864	2.934	4.559
S_2SapH **P***25*	2.759	3.026	4.133
S_2SapH **I***27*	2.984	2.839	4.548
S_2SapH **P***27*	2.928	2.879	4.311
S_2SapH **P***27*[b]	2.919	2.871	4.421
$SapH_52+$ [c]	3.283	3.402	5.233
S_2TPSH[d]	2.835	2.911	4.346

[a] DFT optimized in the 6−31G basis set unless marked differently. [b] DFT optimized in the 6-31G* basis set. [c] Dication of 2,7,18,23-tetramethyl-3,8,12,13,17,22-hexaethylsapphyrin, from ref 27. [d] From ref 19.

substantial planar and inverted structural modifications which are characteristic of 26,28-diheterosapphyrins.

The analysis of the geometrical parameters, gathered at Figures 1−4, has demonstrated that the largest differences for the bond lengths are in the range of few hundreds of angstroms between inverted and planar geometries and that they are practically independent of the tautomer. Generally, the geometrical parameters determined for the planar structures are in the range found for the dicationic sapphyrin[29] and S_2TPSH.[19] The substantial geometrical changes due to the rotation of the C pyrrole, have been noted only for the C(8)C(9)C(10), C(9)C(10)C(11), and C(10)C(11)C(12) bond angles, i.e., for the fragment directly involved in the rearrangement (Table 2). For instance, in the case of the dioxasapphyrin the hypothetical **P***25* → **I***25* transfer would increase the C(8)C(9)C(10) and C(10)-C(11)C(12) angles by 10.2° and 7.7°, respectively. The alteration in the opposite direction, ca. 9°, should be expected for the C(9)C(10)C(11) fragment.

TABLE 4: Calculated Relative Energies[a]

	26,28-dioxasapphyrin		26,28-dithiasapphyrin	
form	B3LYP/6-31G	B3LYP/6-31G**//6-31G	B3LYP/6-31G	B3LYP/6-31G**//6-31G
I*25*	0.816	2.071	32.07	30.372
P*25*	0	0	0	0
P*27*	5.459	5.146	8.095	7.279
I*27*	12.111	12.801	40.600	37.462

[a] In kcal/mol with respect to **P***25*.

The N(25)···N(29), N(25)···X(26) and X(26)···X(28) distances, which describe the trapezoidal shape and the size of the central diheterosapphyrin core for each considered structure, are collected in Table 3. The impact of the C pyrrole ring rotation is mainly reflected by the increase of the X(26)···X(28)

TABLE 5: Rearrangement Energy[a]

		26,28-dioxasapphyrin		26,28-dithiasapphyrin	
fundamental form	rearrangement product	B3LYP/6- 31G	B3LYP/6- 31G//6-31G	B3LYP/6- 31G	B3LYP/6- 31G//6-31G
I*25*	**I***27*	11.295	10.730	8.534	7.091
P*25*	**I***25*	0.816	2.071	32.066	30.372
P*25*	**P***27*	5.495	5.147	8.095	7.279
P*27*	**I***27*	6.652	7.656	32.505	30.183

[a] In kcal/mol.

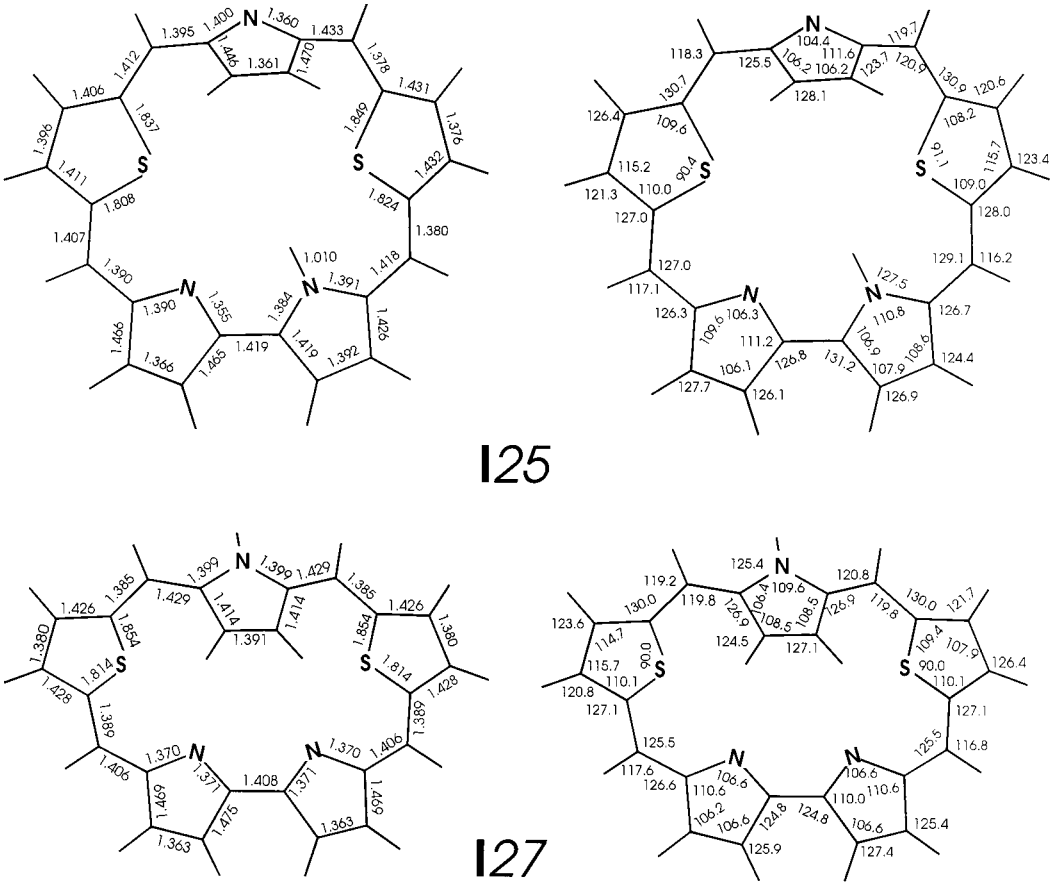


Figure 3. Calculated B3LYP/6-31G geometries of 26,28-dithiasapphyrin **I***25* and 26,28-dithiasapphyrin **I***27*. Bond lengths are in angstroms and the bond angles are in degrees.

separation: O_2SapH, **P***25* → **I***25*, 0.4 Å; **P***27* → **I***27*, 0.5 Å; S_2SapH, **P***25* → **I***25*, 0.4 Å; **P***27* → **I***27*, 0.2 Å. The other interatomic distances vary in the considerably smaller range of 0.15 Å.

The representative examples of the sapphyrin skeleton geometries, i.e., the planar and inverted one, are shown in Figure 5. The position of the C pyrrole ring is apparent in the side view of the inverted geometry. The structures are presented for O_2SapH **I***25* and S_2SapH **P***25*. They are pertinent for the most stable forms of O_2TPSH and S_2TPSH detected by ^{1}H NMR.[18] In the case of the inverted structure, the folding is clearly defined by the C(9)C(10)C(11)C(12) dihedral angles which are equal, respectively: O_2SapH **I***25*, 17.6°; O_2SapH **I***27*, 10.5°; S_2SapH **I***25*, 28.4° and S_2SapH **I***27*, 38.7°, as determined from the DFT optimized structures.

The calculated total energies, using the B3LYP/6-31G**// B3LYP/6-31G approach,[28] are presented in Table 4. The relative stability of the postulated forms decreases in the order of **P***25* > **I***25* > **P***27* > **I***27* for O_2SapH and **P***25* > **P***27* ≫ **I***25* > **I***27* for S_2SapH. By means of ^{1}H NMR we have previously[18] determined the structures of the fundamental tautomers of 5,10,15,20-tetraphenyl-26,28-diheterosapphyrins, namely, **I***25* for O_2TPSH and **P***25* for S_2TPSH. Thus, the present DFT studies do reproduce properly the basic geometry and the localization of the mobile proton for the S_2TPSH tautomer of the lowest energy. In this case the formation of the inverted 26,28-dithiaporphyrin structure is strongly energetically disfavored (ca. 30 kcal/mol). Contrary to 26,28-dithiasapphyrin, both extreme geometries are energetically accessible for 26,28-dioxasapphyrin according to the DFT calculations, although the ^{1}H NMR evidence for O_2TPSH confirms the exclusive presence of **I***25*.[18] However, the **P***25* form of O_2SapH is only slightly more stable in the DFT studies, as the energy difference between **P***25* and **I***25* equals 2 kcal/mol. Here, one has to keep in mind that our calculations offer only an evaluation of the gas-phase energy of meso-unsubstituted structures. Therefore, the real preference in solution may be finally tuned particularly for O_2SapH by other factors, not directly included in calculations.

Recently, we have determined, using the DFT approach, that the inverted form of the sapphyrin dication ($SapH_5^{2+}$) is only slightly less stable than the planar one. The dimethylation of the C pyrrole ring to produce 12,13-dimethylsapphyrin (12,13-

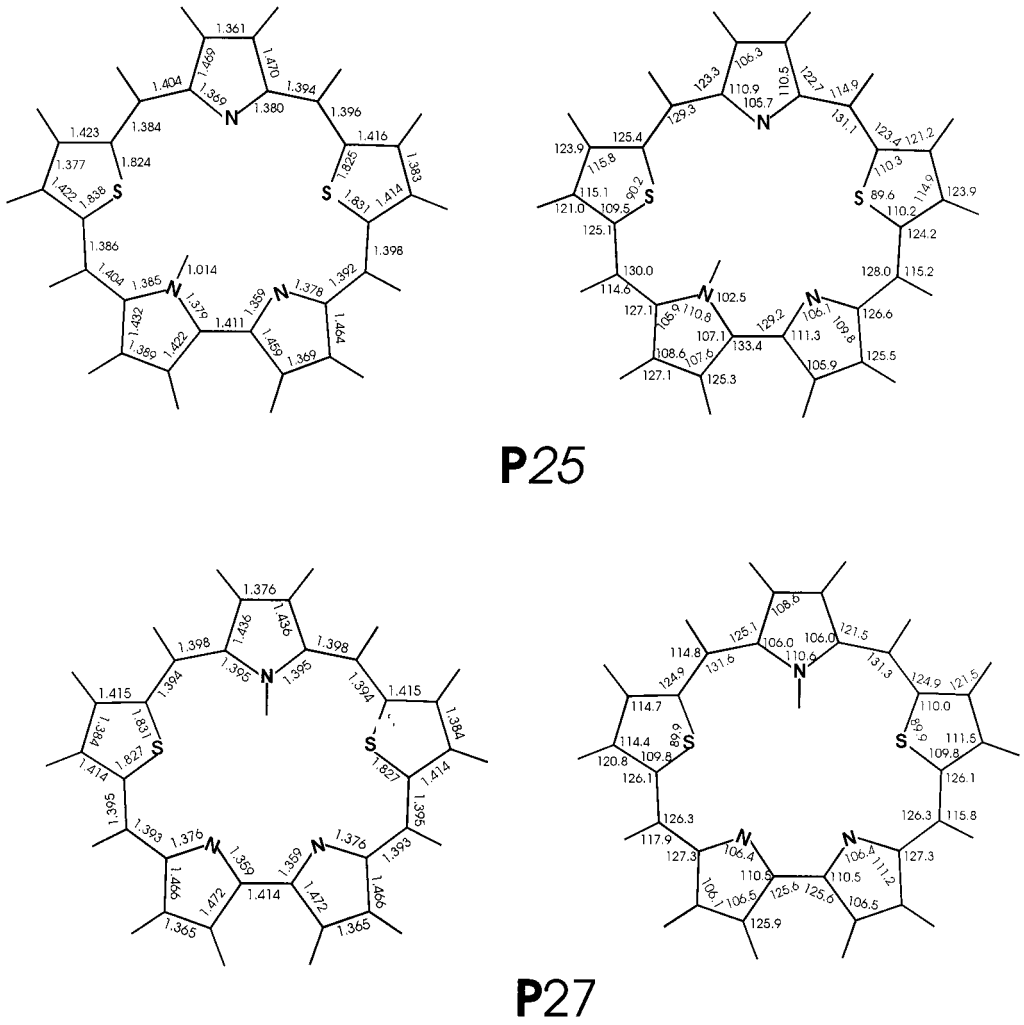


Figure 4. Calculated B3LYP/6-31G geometries of 26,28-dithiasapphyrin **P***25* and 26,28-dithiasapphyrin **P***27*. Bond lengths are in angstroms and the bond angles are in degrees.

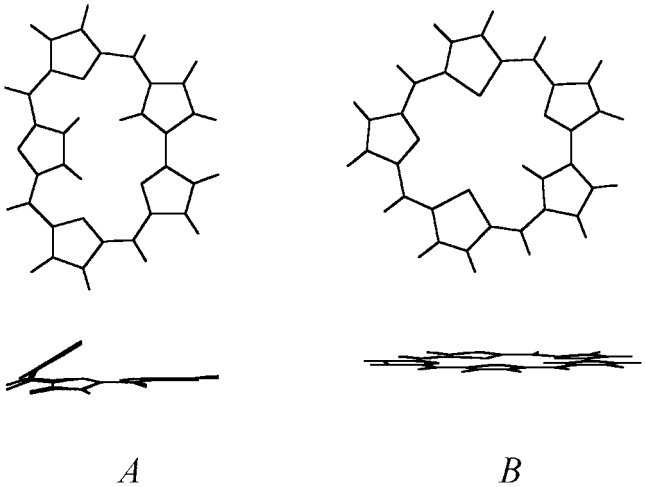


Figure 5. Drawing of the **I***25* and **P***25* structures obtained from DFT calculations for O_2SapH and S_2Sap, respctively. Projections emphasize the difference of the C pyrrole arrangements in both forms. The dihedral angles, C(9)−C(10)−C(11)−C(12), which equal 17.6° for O_2TPSH (**I***25*), and 0°for S_2TPSH (**P***25*) respectively, reflect the distortion of macrocycles.

$DMSapH_5^{2+}$) increased markedly the relative stability of the planar structure. However, a formal rearrangement of 12,13-$DMSapH_5^{2+}$ to generate the isomeric 10,15-dimethylsapphyrin dication (10,15-$DMSapH_5^{2+}$) reversed the stability order (**I***25* > **P***25*). Definitely, the meso-substitution favored the inverted structure of the sapphyrin skeleton.[33] Analogously, the presence of the bulky aromatic meso-substituents can determine the preference for the inverted structure for O_2TPSH despite the **P***25* geometry resulting from the DFT optimization for O_2SapH.

The following sequence of one-proton step processes may be involved in the NH tautomeric equilibria of 26,28-diheteroporphyrin, assuming the preservation of the overall macrocycle structure in the course of the process.

$$\mathbf{P}25 \rightleftharpoons \mathbf{P}29$$

$$\mathbf{P}25 \rightleftharpoons \mathbf{P}27$$

$$\mathbf{P}29 \rightleftharpoons \mathbf{P}27$$

or

$$\mathbf{I}25 \rightleftharpoons \mathbf{I}29$$

$$\mathbf{I}25 \rightleftharpoons \mathbf{I}27$$

$$\mathbf{I}29 \rightleftharpoons \mathbf{I}27$$

Considering the relative stability of diheteroporphyrin tautomers (Table 5), the localization of the proton on the bipyrrolic fragment is strongly preferred in each case. The tautomerisation has a small effect on the bond lengths (Figures 1−4). Conse-

quently, one can assume that the preference for O_2SapH **I***25* and S_2SapH **P***25* over their **I***27* or **P***27* counterparts may be controlled by the moderate effects, namely, by the hydrogen bonding and lone pair−lone pair pyrrole nitrogen, oxygen, or sulfur repulsions.[24] The conceivable N(25)−H···N(29) hydrogen bond influence is expected to be very weak in both discussed systems as the calculated H···N(29) distances are relatively long: O_2SapH **I***25*, 2.849 Å; O_2SapH **P***25*, 2.648 Å; S_2SapH **I***27*, 2.581 Å; S_2SapH **P***25*, 2.533 Å. The other electrostatic factor may be of importance. The **I***27* or **P***27* tautomers would be destabilized by the electrostatic repulsion between two adjacent imino nitrogens lone pair donors located on the bipyrrole unit. The effect would be significant only for **P***27* or **I***27* tautomers. As a matter of fact, some elongations of the N(26)···N(29) distances have been noticed comparing **I***25*/**I***27* (0.12 Å) and **P***25*/**P***27* (0.17 Å) tautomers of S_2SapH. Considering the flexibility of the sapphyrin macrocycle, the alternative long-range steric effect due to the N(27)H···X interaction(s) can be instrumental in the determination of this distance as well.

The calculated energy differences between O_2SapH **I***25*−**I***27* (10.7 kcal/mol) and S_2SapH **P***25*−**P***27* (7.3 kcal/mol) (Table 5) brings a problem of a contribution in equilibrium of the less stable tautomer and raises the question of their simultaneous spectroscopic detection. At present, the ^{1}H NMR evidence for O_2TPSH and S_2TPSH supports exclusively the appearance of a single species.[18] These observations are consistent with the relative energy of the tautomers. In the relevant comparison, the exchange of NH protons of regular porphyrin involves two fundamental tautomeric structures, trans and cis. The recently calculated energy of the cis tautomer with respect to the trans one equals ca. 6−11 kcal/mol.[20b,d] Despite the small difference in stability, the cis porphyrin structure remains to be directly spectroscopically observed. On the other hand, tautomerism of hemiporphycene involves two trans NH tautomeric species which are different in energy, according to DFT calculations, by 0.7 kcal/mol.[24] The splitting of ^{1}H NMR NH resonances at low temperatures confirmed a contribution of two tautomers species in remaining in the dynamic exchange.[34]

In conclusion, the DFT studies have demonstrated that the nature of heteroatoms seems to be essential in stabilization of the inverted and planar structures of 26,28-diheteroporphyrins. Accordingly, the large sulfur atoms promote solely the planar arrangement. The smaller size of the two oxygen atoms seems to stabilize comparably both the inverted and planar structures. Although some of the hypothetical 26,28-diheterosapphyrin forms have not been experimentally observed, the DFT calculations revealed their relative stabilities and provided some insight into the energy required for the tautomerization process.

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