

Theoretical Analysis on Molecular Magnetic Properties of *N*-Confused Porphyrins and Its Derivatives

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We have theoretically investigated the magnetic properties of *N*-confused porphyrin (NCP), tetraphenyl-*N*-confused porphyrin (TPNCP) and their substituted derivatives with O, S and Se heteroatoms (2ONCP, 2STPNCP, 2SeNCP, 2OTPNCP, etc.) by using DFT method. In the minimum energy structures of the 2OTPNCP, the two couples opposite phenyl substitutes are staggered. In the case of TPNCP, 2STPNCP and 2SeTPNCP, two phenyls being respectively close to or opposite to *N*-confused pyrrole are found to be pointed the same direction, whilst others are in the opposite direction. Based on the equilibrium structures, the ¹H chemical shifts and nucleus-independent chemical shifts (NICS) are calculated in this paper. The π current density being induced by the tridimensional perpendicular magnetic field transmits the inner section of the pyrrole segments for NCP and TPNCP. As for their substituted derivatives with O, S and Se atoms, the current path passes through the outer section of the two heterorings. The NICS values at the ring critical points of the heterorings are much lower (in absolute value) than those of which is at the center of an isolated pyrrole molecule. The ¹H NMR for β H atoms of the heterorings decreases from O, S to with Se.

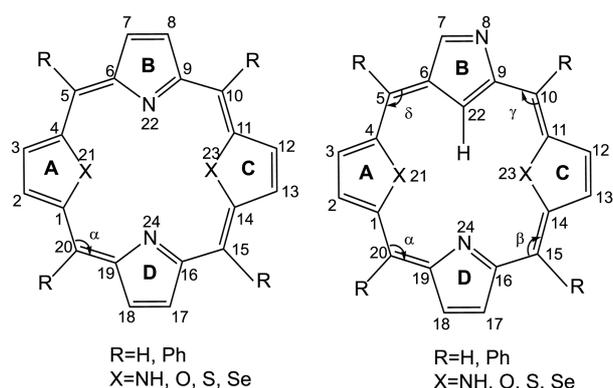
Key Words : Heteroporphyrins, Hetero-*N*-confused porphyrins, NICS, π current density, ¹H NMR

Introduction

Aromaticity has been used in chemical literature frequently.¹ The history of this concept has begun with the isolation of benzene by Michael Faraday in 1825.^{2,3} The Hückel rule⁴ is the most popular theory to define the aromaticity of compounds. According to this rule, [4n] π -electron conjugated molecules have a closed-shell electron configuration, and are deemed to possess antiaromatic character. In contrast with Hückel's consideration of planar molecular structures, Heilbronner suggested that [4n] π -electron conjugated systems could form a closed-shell configuration – and thus also be aromatic – when the system adopts a Möbius-strip-like topology with a half-twisted π surface (or a more twisted form with an odd number of half-twists).⁵ ¹H NMR chemical shifts as well as magnetic susceptibility anisotropies are the most widely used general criteria for characterizing the aromaticity and antiaromaticity of compounds. Subsequently, nucleus independent chemical shift (NICS) is, being proposed by Schleyer *et al.*⁶ as a simple and efficient aromaticity criterion, still used in both organic⁷⁻⁹ and inorganic compounds.¹⁰ Respective positive, negative and zero values of NICS denote antiaromaticity, aromaticity and nonaromaticity. With the continuous emergence of a great deal of compounds, the concept of aromatic complexes is, to date, beyond the conventional limitation, thus expanding to other chemical materials, such as the non-benzene compounds, the ion and the heterocyclic compounds.¹¹ To our best knowledge, no general definition for aromaticity, however, is established yet due to lack of an

observable quantity. Besides, aromatic molecules have distinguishing features in the NMR spectra such as thermodynamic stability and diatropic ring currents on structural perimeter.¹²

Porphyrins have been studied experimentally and theoretically during the past decades¹³⁻²⁰ in respect of their practical applications in biology,²¹ coordination chemistry²² and optical power limiting.²³⁻²⁷ Porphyrins belong to highly conjugated macrocycles being composed of four modified pyrrole subunits with the linkage of methine bridges (=CH-) between α carbon atoms. Porphyrins are aromatic on the magnetic criterion. The system is aromatic if the ring current has the diatropic sense. The NICS values are utilized to determine whether the π system of the molecule has pyrrole ring currents and the internal cross. The aromatic pathway must be considered to be a superposition of mainly the 22 π - and 26 π -electron paths.²⁸ The analysis of induced ring currents strengths has also shown that, as for porphyrin, its pyrrole rings lacking an inner hydrogen atom (The NH was displaced by isoelectronic O, S, Se *etc.*) have relatively lower ring current than others with an inner hydrogen atom.²⁹ The net result of π current density being located at the HOMO and HOMO-1, is to make the porphyrin ring be a four-electron diamagnetic system.³⁰ For many porphyrin isomers, the *N*-confused porphyrin (NCP) as a pure isomer of porphyrin is unique. It inverses one pyrrole ring in regular porphyrin molecule, which possesses a reactive inner carbon atom and a peripheral nitrogen atom.³¹ Many differences have been discovered between porphyrin and NCP,³²⁻³⁴ such as the one-proton absorption intensities and the difference of



Scheme 1. Atom numbering in porphyrin. **Scheme 2.** Atom numbering in *N*-confused porphyrin.

activation energies.^{17,35} The reason for the alteration can be explained by aromaticity and the 22 π - and 26 π -electron paths.

One general method of studying NCP and hetero-*N*-confused-porphyrins is to replace NH groups of a pyrrole with other donor atoms (O, S and Se). This is because the oxygen atom and the NH group are isoelectronic species. Oxygen, sulfur and selenium atoms belong to the same main group. It can alter the cavity size and electron structure by incorporating heteroatoms into the core of the macrocycle, which provides interesting spectroscopic, chemical and physical properties caused by different aromaticity.^{27(b), 36-38}

In this work, we carried out a theoretical analysis on the effect of *N*-confused isomerization and substitution of pyrrole NH groups by O, S and Se heteroatoms on the molecular magnetic properties of NCP and tetraphenyl-*N*-confused porphyrin (TPNCP). We performed a comparative study on porphyrin (P), tetraphenylporphyrin (TPP), NCP, TPNCP and their diheteroatom substituted derivatives where NH groups of pyrrole are replaced by O, S and Se heteroatoms (2OP, 2SP, 2SeP, 2OTPP, 2STPP, 2SeTTP, 2ONCP, 2SNCP, 2SeNCP, 2OTPNCP, 2STPNCP and 2SeTPNCP), based on the NICS, ¹H NMR chemical shifts and NBO analysis results (for atom numbering see Scheme 1 and

Scheme 2).

Computational Details. Full geometry optimizations are performed by employing the density functional theory³⁹ method based on Becke's three parameter hybrid functional and gradient-corrected correlation functional of Lee *et al.* (B3LYP)⁴⁰⁻⁴² with *Gaussian09* program package.⁴³ The 6-31+G (3df, 3pd) basis set is employed to calculate selenium atom, and the 6-31G (d) basis set is used to calculate the other atoms. Vibrational frequencies of all the studied structures are calculated at the same theory level, which is characterizing all of them as minima on the corresponding potential energy surfaces. An NBO analysis⁴⁴ is also performed at the B3LYP/6-31G (d) theory level except for the geometry containing selenium atom at the B3LYP/6-31+G (3df, 3pd) theory level.

The ¹H chemical shifts (taking TMS as a reference) are computed. The electron density is analyzed by means of the 'atoms in molecules' theory of Bader⁴⁵ using the AIM2000 package. The nucleus-independent chemical shifts (NICS)⁴⁶ are calculated at the *N*-confused porphyrin center and at the (3, +1) ring critical points of the four pyrrole rings. NICS is an aromaticity index through the GIAO (Gauge-Independent Atomic Orbital) method at the B3LYP/6-311+G (2d, p) theory level for NCP, 2ONCP and 2SNCP, at the B3LYP/6-31+G (3df, 3pd) theory level for 2SeNCP, 2SeTPNCP, and at the B3LYP/6-31+G (d) theory level for TPNCP, 2OTPNCP and 2STPNCP.

Results and Discussion

The most important geometrical parameters obtained through optimization of the heteroporphyrins, hetero-NCPs, heterotetraphenylporphyrins, and heterotetraphenyl-*N*-confused porphyrins are listed in Table 1 and Table 3. The π -currents induced by the magnetic field for hetero-NCPs and TPNCPs are presented in Figure 1 and Figure 2. As seen from Figure 1 and Figure 2, the π current density exhibits similar structures in the case of hetero-NCPs and TPNCPs. The colors are just used to make the figures to be distin-

Table 1. Most important geometrical parameters of the optimized Porphyrin, P, and their 21,23-diheteroatom (O, S, Se) substituted derivatives, 2OP, 2SP, 2SeP; *N*-confused porphyrin NCP, and their 21,23-diheteroatom (O, S, Se) substituted derivatives, 2ONCP, 2SNCP, 2SeNCP. See Scheme 1 and Scheme 2 for definition of α , β , γ , δ angles

System	N22–N24 distance/Å	C2–C13 distance/Å	C5–C6 distance/Å	C9–C10 distance/Å	α /°			
P ^a	4.059	8.521	1.399	1.399	127.1			
2OP ^a	4.011	8.549	1.401	1.401	129.0			
2SP ^a	4.649	8.096	1.408	1.408	125.2			
2SeP ^a	4.707	8.118	1.414	1.414	125.0			
System	N22–N24 distance/Å	C2–C13 distance/Å	C5–C6 distance/Å	C9–C10 distance/Å	α /°	β /°	γ /°	δ /°
NCP	4.006	8.651	1.403	1.397	127.6	127.6	125.4	125.2
2ONCP	3.799	8.692	1.402	1.393	129.6	129.6	126.3	125.9
2SNCP	4.740	8.175	1.412	1.403	125.5	125.5	124.5	124.4
2SeNCP	4.875	8.086	1.417	1.410	125.4	124.9	124.2	124.1

^aThe values from Ref. 29 and our recalculated.

Table 2. ^1H NMR shifts and NICS values for **P**, **2OP**, **2SP**, **NCP**, **2ONCP**, **2SNCP** at the B3LYP/6-311+G (2d, p), for **2SeP** and **2SeNCP** at the B3LYP/6-311+G (2d, p). For ^1H shifts TMS (31.82) has been taken as a reference at the same theory level

	P ^a	2OP ^a	2SP ^a	2SeP ^a
^1H NMR β -heterocycle proton (ppm)	10.01	10.34	10.67	10.68
NICS				
A and C ring critical points	-12.01	-15.54	-14.86	-13.37
B and D ring critical points	-2.04	2.21	-0.70	-0.84
Porphyrin ring center	-14.98	-15.54	-15.94	-16.88
	NCP	2ONCP	2SNCP	2SeNCP
^1H NMR β -heterocycle proton (ppm)	9.56	9.87	10.22	10.38
NICS				
A ring critical points	-12.14	-14.83	-14.71	-14.66
C ring critical points	-12.35	-15.77	-15.67	-14.85
B ring critical points	3.45	11.11	4.94	2.53
D ring critical points	-2.25	1.30	0.28	-0.80
<i>N</i> -confused porphyrin ring center	-13.63	-14.00	-14.81	-15.94

^aThe values from Ref. 29 and our recalculated.**Table 3.** Most important geometrical parameters of the optimized tetraphenylporphyrin, **TPP**, and their 21,23-diheteroatom (O, S, Se) substituted derivatives, **2OTPP**, **2STPP**, **2SeTPP**; tetraphenyl-*N*-confused porphyrin **TPNCP**, and their 21,23-diheteroatom (O, S, Se) substituted derivatives, **2OTPNCP**, **2STPNCP**, **2SeTPNCP**

System	N22–N24 distance/Å	C2–C13 distance/Å	C5–C6 distance/Å	C9–C10 distance/Å	$\alpha/^\circ$			
TPP ^a	4.077	8.507	1.411	1.411	125.3			
2OTPP ^a	4.030	8.535	1.412	1.412	127.2			
2STPP ^a	4.654	8.089	1.419	1.412	123.4			
2SeTPP ^a	4.728	8.127	1.412	1.412	123.4			
System	N22–N24 distance/Å	C2–C13 distance/Å	C5–C6 distance/Å	C9–C10 distance/Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	$\delta/^\circ$
TPNCP	4.032	8.573	1.418	1.412	125.6	125.7	122.2	122.9
2OTPNCP	3.828	8.654	1.415	1.407	127.4	127.4	123.7	123.9
2STPNCP	4.732	8.140	1.429	1.417	123.5	123.8	121.1	121.9
2SeTPNCP	4.832	8.004	1.435	1.427	122.6	123.3	120.7	121.3

^aThe values from Ref. 29 and our recalculated.

guished. Table 2 and Table 4 collect the calculated data of the porphyrins, *N*-confused porphyrins, tetraphenylporphyrins and the tetraphenyl-*N*-confused porphyrins in terms of the ^1H shifts and NICS values.

In comparing the **P** and **NCP**, **2OP** and **2ONCP**, the longer C2–C13 length and shorter N22–N24 length are found as one pyrrole fragment isomerized to form **NCP**. The distances of C5–C6 and C9–C10 in **Ps** have the same values,²⁹ which are smaller and bigger than corresponding **NCPs**, respectively. In contrast to **NCP**, it provokes an increase in the N22–N24 distance and a decrease in the C2–C13 distance of 0.73 Å and -0.48 Å for **2SNCP**, and of 0.87 Å and -0.57 Å for **2SeNCP**, respectively, due to the presence of S or Se heteroatoms. These suggest the effect on geometry variation of introduced heteroatom with longer atomic radii is more forceful than that of pyrrole isomerization. The C–C (*meso*)–C angles change from 127.6° in **NCP** to 125.5° in **2SNCP** and 125.4° in **2SeNCP**. The corresponding γ and δ angles in **NCPs** all turn smaller than α and β angles (see Table 1). This mutual approach of the two heterocycles in **2SNCP** and

2SeNCP can be understood by taking into account the results of an analysis of the π electron density which is by means of the ‘atoms in molecules’ theory of Bader. Actually, in **NCP** and **2ONCP** the ring center corresponds to a (3, +1) ring critical point with ρ values of 0.0055 and 0.0016 au, respectively, whereas in **2SNCP** and **2SeNCP** present at the ring center at (3, -1) bond critical point with ρ values of 0.0140 and 0.0210 au respectively, which is consistent with a stabilizing interaction between the two heteroatoms S and Se. This implies that the bigger of ρ values are, the closer of four rings in **NCPs** are.

On the other hand, it demonstrates that in **NCP** there is an important stabilizing interaction (second order perturbation energies of 41 kcal/mol) between the lone pairs on the nitrogen atom of the pyrrole NHs and the two closer *meso* π antibonding C–Cs, whereas in **2ONCP**, **2SNCP** and **2SeNCP** the stabilizing interaction of the heteroatom lone pairs with the neighboring π antibonding C–Cs is much weaker (about 27, 21 and 18 kcal/mol, respectively), which is a consequence of a poorer overlap by the NBO analysis. This

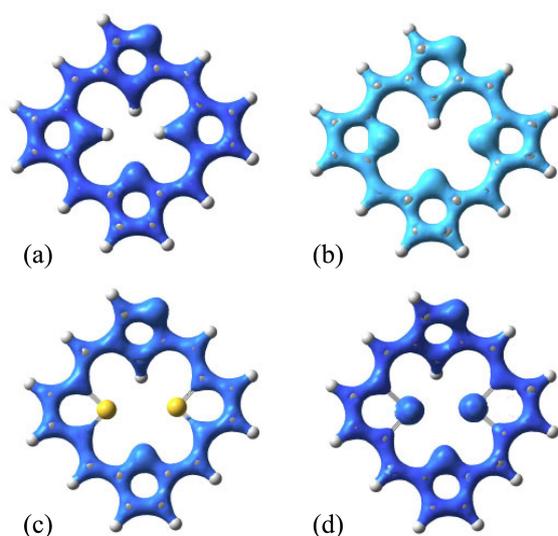


Figure 1. Current density maps for the π electron distribution of: (a) *N*-confused porphyrin; (b) 21,23-dioxa-*N*-confused porphyrin; (c) 21,23-dithia-*N*-confused porphyrin; (d) 21,23-diselena-*N*-confused porphyrin.

reveals that the O, S and Se lone pairs in the heteroporphyrins and hetero-NCPs present a lower mobility compared with that of the N lone pairs of the pyrrole NHs in NCP.

This diminution in the interaction strength between the heteroatom lone pairs and the π antibonding C–Cs in heteroporphyrins is clearly reflected in the current density maps. The magnitude and the direction of the current density induced in the mobile π electrons by magnetic field are presented in Figure 1. The current densities displayed in these figures are evaluated at the 1 bohr height above the molecular plane. For NCPs and hetero-NCPs, the main contributions to the current density for heteroporphyrins come from HOMO and HOMO-1. The current diverges from the four pyrrole rings, so there is no local ring current through them. Figure 1 shows that the presence of the hetero-

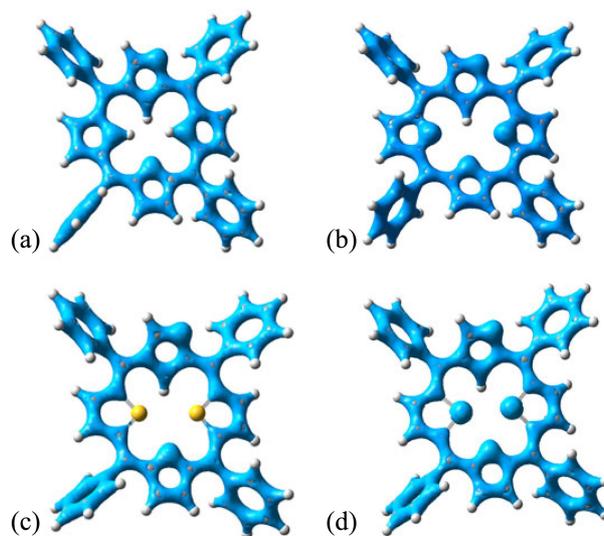


Figure 2. Current density maps for the π electron distribution of: (a) *N*-confused tetraphenylporphyrin; (b) 21,23-dioxa-*N*-confused tetraphenylporphyrin; (c) 21,23-dithia-*N*-confused tetraphenylporphyrin; (d) 21,23-diselena-*N*-confused tetraphenylporphyrin.

atoms arouses a decrease in the current density through the inner section of rings A and C owing to the lower mobility of their lone pairs. This effect is particularly important in cases of 2SNCP and 2SeNCP. The maximum current density through the hetero atom sections of N, O, S as well as Se are 10^{-2} , 10^{-2} , 10^{-3} and 10^{-5} levels for NCPs.

The above mentioned current patterns are reflected by the calculated NICS values (see Table 2). The NICS results can be interpreted taking into account the points located in the plane of the molecule outside. The current path through the *N*-confused porphyrin ring is deshielded because of the strong anisotropy of the magnetic susceptibility of the macrocycle. The NICS values at the ring critical points of ring A in NCP (–12.14) and ring C in NCP (–12.35) are at our theory level, and they are much lower in absolute value

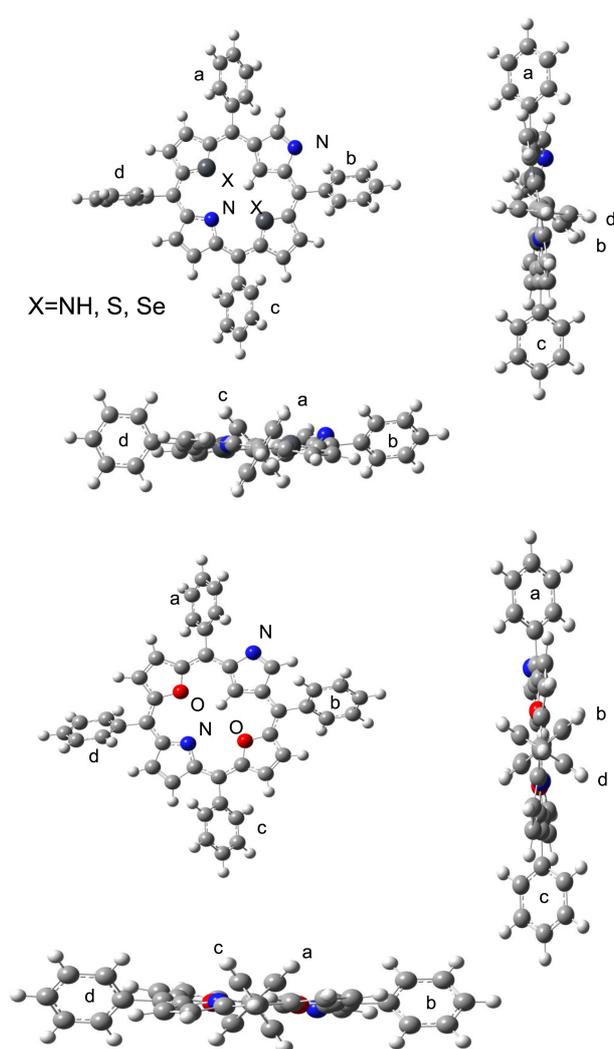
Table 4. ^1H NMR shifts and NICS values for TPP, 2OTPP, 2STPP, TPNC, 2OTPNCP, 2STPNCP at the B3LYP/6-31+G (d), for 2SeTPP and 2SeTPNC at the B3LYP/6-31+G(3df, 3pd) level. For ^1H shifts TMS (32.09) has been taken as a reference at the same theory level. The data in parentheses are experimental values³⁸

	TPP ^a	2OTPP ^a	2STPP ^a	2SeTPP ^a
^1H NMR β -heterocyclic proton (ppm)	8.72 (8.72)	8.92 (9.37)	9.61 (9.63)	9.63 (9.86)
NICS				
A and C ring critical points	–12.72	–16.16	–15.90	–14.70
B and D ring critical points	–2.40	2.37	–0.30	–1.59
Porphyrin ring center	–14.46	–13.80	–15.10	–16.34
	TPNC	2OTPNCP	2STPNCP	2SeTPNC
^1H NMR β -heterocycle proton (ppm)	8.38	8.42	8.98	9.24
NICS				
A ring critical points	–12.49	–16.71	–15.13	–13.88
C ring critical points	–13.37	–17.17	–16.39	–15.75
B ring critical points	1.07	9.49	2.71	1.86
D ring critical points	–2.78	–1.15	–0.09	–0.80
<i>N</i> -confused porphyrin ring center	–12.68	–13.39	–11.94	–10.31

^aThe values from Ref. 29 and our recalculated.

than those at the center of an isolated pyrrole molecule (-19.23). This difference can be attributed to the different distribution of ring current on the inner or outer sides. Ring critical points are outside the current path. In hetero-NCPs, the current density through the inner of rings A and C decreases, while the current density through the outer part reinforces. Therefore, ^1H NMR for the β hydrogen atoms of the heterocycles in hetero-NCPs are smaller than those in NCP, while the NICS values (in absolute value) at the (3, +1) or the (3, -1) ring critical points of these rings in hetero-NCPs are larger than those in NCP (see Table 2). From **2ONCP** to **2SeNCP**, the NICS values at the ring critical points of rings A and C decrease in absolute value, which is probably owing to the above mentioned deformation of the macrocyclic internal cross caused by the interaction between two S and Se heteroatoms. The NICS values at the ring critical points of rings B and D, on the other hand, show much smaller absolute values than those for rings A and C. Because of that rings B and D locate outside the main current path. They are deshielded. Finally, the NICS values at the ring center increase apparently in absolute value from **2ONCP** to **2SeNCP**. This fact could be caused by the deformation of the macrocycle internal cross. The NICS values at the ring center for **P**, **2OP**, **2SP**, **2SeP**²⁹ are larger than those at NCP, **2ONCP**, **2SNCP**, **2SeNCP** in absolute value, respectively. The tendency of the aromatic reduction is also reflected by relaxation of molecular geometry and weaker electron density results.

The optimized tetraphenyl-NCPs display a small deviation from NCP ring with planarity, except for **2OTPNCP** which presents a standard NCP plane. In **TPNCP**, **2STPNCP** and **2SeTPNCP**, the two hetero atoms and the N atom of pyrrole ring define a plane. The N atom of *N*-confused pyrrole ring is located above this plane, while the β C atom of the *N*-confused pyrrole ring is situated slightly under this plane. The four *meso* phenyl groups are not at right angles to the plane of NCP ring but slant from this position about 43° (**TPNCP**), 37° (**2OTPNCP**), 46° (**2STPNCP**) and 54° (**2SeTPNCP**). The swing angles of phenyl groups at NCP are much larger than those at **P** ring. From the structural character, the fine aggregation behavior does not appear in **TPNCPs**. As for **2OTPNCP**, the two couples of opposite phenyl substitutes are staggered, while for **TPNCP**, **2STPNCP** and **2SeTPNCP**, the phenyl which is close to *N*-confused pyrrole and the opposite phenyl slant to the same direction and the other phenyls slant to the inverse direction (see Scheme 3). As in the cases of the hetero-NCP, the presence of the two heteroatoms S and Se in **2STPNCP** and **2SeTPNCP** causes an important distortion, which is owing to the interaction of two S atoms or two Se atoms (S-S and Se-Se bond critical points are located with ρ values of 0.0134 and 0.0258 au, respectively). The N22-N24 length increases 0.70 Å for **2STPNCP**, and 0.80 Å for **2SeTPNCP** in contrast with the **TPNCP**. The C2-C13 length decrease 0.43 Å for **2STPNCP**, 0.57 Å for **2SeTPNCP** compared with the **TPNCP** (see Table 3). The N22-N24 length and the C2-C13 length in **2STPNCP** are all longer than that in **2STPP**. For **2SeTPNCP**,



Scheme 3

the N22-N24 length becomes the longest to form the gracile geometry and the C2-C13 length is shorter than that in **2SeTPP**.²⁹

An NBO analysis shows that the important stabilizing interaction between the lone pairs on the nitrogen atoms of the pyrrole moieties toward inside forms the *meso* π anti-bonding C-Cs in **TPNCPs**. The important stabilizing interaction in **TPNCP** (43 kcal/mol) is larger than that in **2OTPNCP** (28 kcal/mol), and **2STPNCP** (23 kcal/mol), and **2SeTPNCP** (19 kcal/mol). It is due to the involved heteroatoms which diminish the mobility of these electrons. In agreement with this, the maps of the π current density of **TPNCP**, **2OTPNCP**, **2STPNCP** and **2SeTPNCP** are analogous to the unsubstituted systems (see Figure 2).

The NICS values (see Table 4) at rings A and C, B and D, and at the center of the **P** ring and NCP ring are analogous to those for the heteroporphyrins and hetero-NCPs. However, the NICS at the porphyrin center for **2OTPP** is smaller in absolute value than that for **TPP**. For **2STPNCP** and **2SeTPNCP**, the NICS at the NCP center are now smaller in absolute value than those for **TPNCP**.²⁹ ^1H NMR of the heterocyclopentadiene moieties presents appreciable down-

field shifts, which is in good agreement with the reported experimental data.³⁸

Conclusion

The *N*-confused heteroporphyrin notably distorts the originally unsubstituted macrocycle geometries due to the existence of S–S and Se–Se interactions. The two couples of opposite phenyl substitutes are also staggered in the case of **2OTPNCP**, while two phenyls respectively being close to or opposite to *N*-confused pyrrole point to the same direction and the other phenyls are tilted to the opposite direction in the case of **TPNCP**, **2STPNCP** and **2SeTPNCP**. For **NCP** and **TPNCP**, the π current crosses the inner section of the pyrrole subunits. However, the presence of O, S and Se heteroatoms in 21,23-diheteroporphyrins leads to the decrease in the current density crossing the outer section of the two heterorings. The NICS values at the ring critical points of the heterorings are much lower (in absolute value) than that at the center of an isolated pyrrole molecule. The NICS values at the ring critical points of the **NCPs** are smaller than those gotten from **Ps** in some sort. The ¹H NMR presents appreciable downfield shifts for the β H atoms of the heterorings in the 21,23-heterosubstituted molecules and it is excellent agreement with the reported experimental data.

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