# Aromaticity in tautomers of triazoleporphyrazine

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The effect of tautomerism on the aromaticity was studied for the free base triazoleporphyrazine at the Density Functional Theory level, using double-zeta double polarized basis sets. The porphyrazine (**1**), the three tautomers (**2a**, **2b** and **2c**) as well as the Ni complex (**3**) of triazoleporphyrazine were examined. Two independent aromaticity criteria, the geometry-based index HOMA and the magnetic properties-based index NICS, were used to estimate the aromaticity of the complete and selected fragments of the above compounds. Results show that structure **2a**, which has the H atom in position 1 of the triazole ring, has low aromaticity, although it contains structural fragments with large conjugation. The aromatic character of both tautomers **2b** and **2c** is similar to that of both the porphyrin and the porphyrazine. The central ring contour was found to be the most aromatic part of the triazoleporphyrazine tautomers. Occupancy of the central position of the macrocycle cavity of the triazoleporphyrazine by a metal atom increases the aromaticity of the macrocycle as a whole, but reduces the conjugation of the *central cross* sub-unit. In conclusion, both criteria can be used confidently for evaluating the aromaticity for the studied systems.

## 1 Introduction

The porphyrins play an outstanding biological role in the processes of respiration and photosynthesis,[1,2] whereas the phthalocyanines have many applications as dies and catalysts.[3] Other interesting properties of both classes of compounds have also been studied.[1–3] Recent studies focused on noncentrosymmetrical phthalocyanines and related compounds have determined the nonlinear optical properties of those compounds and have provided the possibility of building supramolecular organized systems by the Langmuir–Blodgett technique.[3–5] This, in turn, opens many possibilities for the practical application of these compounds.

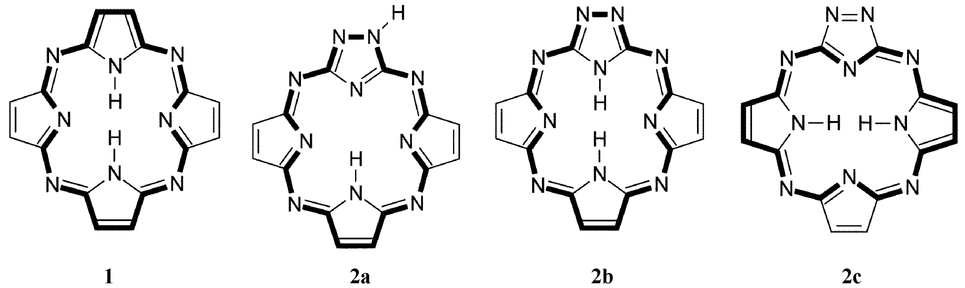
The application of these compounds to any of the fields indicated above strongly depends on the electronic structure of their macrocyclic units. As regards the electronic structure of the macrocycle, its aromaticity has an outstanding importance.

One of the most efficient methods to obtain noncentrosymmetrical phthalocyanines and other related compounds is the formal substitution of one of the isoindole fragments of the phthalocyanine molecule by a heteroaromatic ring. Following this strategy, triazolephthalocyanines[6] and thiadiazolephthalocyanines[7] were synthesized. New classes of azaporphyrin unsymmetrical analogues, namely triazolephthalocyanines[8] and triazoleporphyrazine[9] free bases, were also prepared. On the other hand, theoretical calculations on triazolephthalocyanines are currently available.[10]

Since triazoleporphyrazines are of great interest as a new type of intrinsically noncentrosymmetrical porphyrazine analogue, we report here a theoretical investigation of the electronic structure of the macrocycle, with emphasis on its aromaticity.

## 2 Models and computational methods

Hexa(4-*tert*-butylphenyl)porphyrazine (compound **5** in ref. 9) and its Ni complex (compound **7a** in ref. 9) have been synthesized and experimentally investigated.[9] In order to study the electronic structure of this class of compounds at an adequate theoretical level with reasonable low computational effort, we have selected two model structures: the free-base triazoleporphyrazine and its Ni complex. This approach does not exclude the possibility of the real existence of any of the calculated systems. The free-base triazoleporphyrazine is represented by three tautomeric structures: **2a**, **2b** and **2c** (see Chart 1)



**1** **2a** **2b** **2c**

**Chart 1** Structures of porphyrazine **1** and triazoleporphyrazine tautomers **2a**, **2b** and **2c**. The molecular fragments corresponding to the [18]heteroannulene systems are represented in bold.

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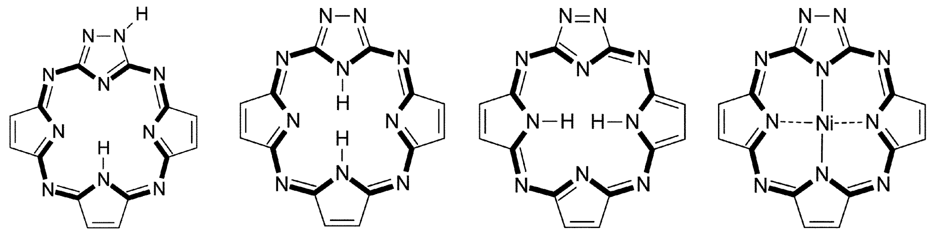


**2a** **2b** **2c** **3**

**Chart 2** *Internal crosses* depicted as bold lines for structures **2a**–**2c** and **3**.

that have either one or two hydrogen atoms in the central macrocyclic cavity. The Ni–triazoleporphyrazine was labeled as **3** (see Chart 2). The described tautomerism corresponds to the proton transfer between nitrogen atoms. Therefore, metal complexes (in which the metal is located at the center of the macrocyclic cavity) do not show this kind of tautomerism.

The triazoleporphyrazine system of conjugation may be considered as a porphyrin-like system perturbed by: i) the introduction of four nitrogen atoms instead of four CH-bridged groups (porphyrazine), and ii) the substitution of one $C_2H_2$ group by N–N (triazoleporphyrazine). Obviously, the tautomerism may produce changes in the conjugation of the triazoleporphyrine molecule. This concretizes the aim of this work.

To our knowledge, the systems in which studies of aromaticity using quantitative criteria have been made[11–15] correspond to two main categories: i) the five- (thiophene, furan, pyrrole, *etc.*) and six- (benzenoid hydrocarbons, their hetero-analogues with N, O, S and P as heteroatoms, *etc.*) membered rings and their fused derivatives, and ii) the porphyrinoid macrocycles in which, invariably, the *meso* positions are occupied by CH groups. The latter of these categories is the one that, on structural grounds, is closest to our systems, although it differs (see above) to a certain extent. No reports about aromaticity index calculations of tetra-aza substituted derivatives have appeared up to now. Taking into account that porphyrazine can be considered the structural "bridge" between the porphyrins and the triazoleporphyrazines, we have also calculated the aromaticity of porphyrazine (labeled as **1** in Chart 1) in order to compare our results with previous reports.

Since the aromaticity may be related to either the whole molecule (total aromaticity) or to one of the molecule sub-units (local aromaticity),[11,12] two structural sub-spaces have been defined here for the studied compounds: i) the [18]heteroannulene fragment (see Chart 1), and, ii) the *internal cross* (see Chart 2). The [18]heteroannulene contour[16] is a molecular subunit composed by 18 atoms containing 18 π electrons which is drawn following the single/double bond alternation, whereas the *internal cross* is a [16]heteroannulene contour also bearing 18 π electrons. It has been found that the *internal cross* is the most aromatic part of the porphyrin molecules.[11,12]

The aromaticity of the described structures was estimated by two quantitative criteria: i) the geometry-based index, namely Harmonic Oscillator Model of Aromaticity (HOMA)[11,12] and ii) the Nucleus Independent Chemical Shifts (NICS).[11,13–15]

The HOMA may be dissected into two components, EN and GEO:

$$\mathrm{HOMA} = 1 - \alpha\left(R_{\mathrm{opt}} - R_{\mathrm{av}}\right)^2 - \frac{\alpha}{n}\sum\left(R_{\mathrm{av}} - R_i\right)^2 = 1 - \mathrm{EN} - \mathrm{GEO}$$

Here, $n$ is the number of bonds taken into the summation, and $a$ is an empirical constant fixed to give HOMA = 0 for the hypothetical Kekule structures of aromatic systems and HOMA = 1 for the systems with all bonds equal to the optimal value $R_{\mathrm{opt}}$. The individual bond lengths are depicted by $R_i$. The quantity $R_{\mathrm{opt}}$ is defined as the length of the C–C bond for which the energy of compression to the length of a single bond in 1,3-butadiene is minimal. $R_{\mathrm{av}}$ is the averaged bond length,

$$R_{\mathrm{av}} = \frac{1}{n}\cdot\sum_{i=1}^{n} R_i$$

The EN term describes changes in aromatic character due to deviations of the average bond length from the optimal value, while the GEO term reflects the consequences of bond length alternation. The corresponding values taken in this work for $a$ and $R_{\mathrm{opt}}$ are reported in ref. 11.

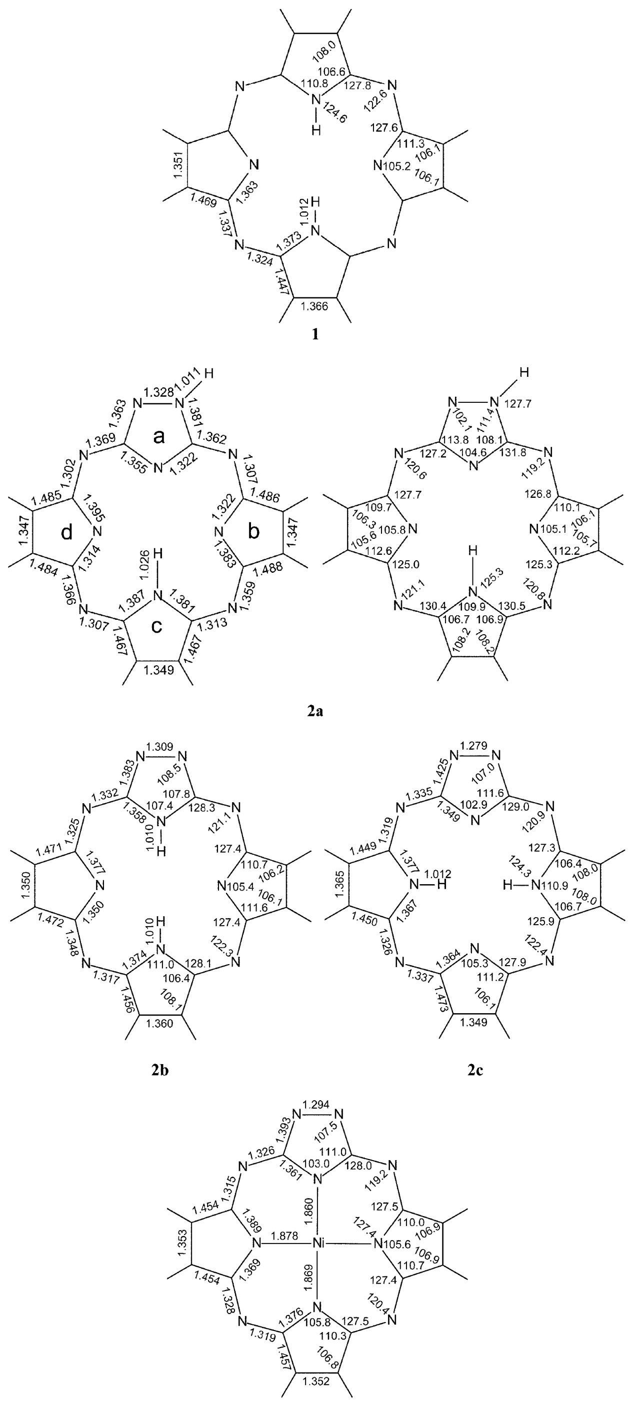
Geometry-based indices provide an appreciation of the aromaticity of the whole molecule as well as the local aromaticity of its fragments. In correspondence with the structural analysis of the studied systems (see above), four main structural arrangements: i) the whole molecule, ii) the [18]heteroannulene sub-unit (see Chart 1), iii) the triazole ring (designated by "a" in Fig. 1), and iv) the *internal cross* (see Chart 2) were considered here.

The NICS indices were introduced by Schleyer *et al.*[13] and are reliable indicators of aromaticity based on the magnetic properties of the atomic nuclei in the molecule. They are defined as the negative value of the absolute shieldings computed at a ring center or some other interesting point in the system. The rings with negative NICS values are classified as aromatic. Hence, more aromatic rings have more negative NICS. Consequently, the antiaromatic systems have positive values of NICS, whereas nearly zero NICS correspond to nonaromatic molecules.

The main advantage of NICS indices is that they do not depend on the choice of a reference molecule. However, NICS calculations show considerable limitations in the selection of the point at which the nuclear shieldings have been calculated. Furthermore, as they are calculated for individual rings, it is very difficult in some cases to distinguish among different rings with approximately the same geometrical center. The NICS calculations, as criteria of aromaticity, are related to the fact that the aromatic compounds have a π electron ring current that is induced when the system is exposed to external magnetic fields. This current increases as the aromaticity of the molecule increases. The Gauge-Independent Atomic Orbital (GIAO) method[17,18] has been used to evaluate NICS indices. They were evaluated in the present work both at the geometrical center of the macrocyclic cavity determined by the pyrrole nitrogens and at the center of the triazole ring as indicated in Fig. 2.

Natural Bond Order (NBO)[19–21] calculations were performed to determine the π electron density (as electron occupancy of the $p_z$ orbitals) on the atoms at different positions. The NBO approach represents the wave function in terms of localized Lewis structures.

The geometry optimization of structures **1**, **2a**–**2c** and **3** as well as the NBO and GIAO calculations were carried out at the DFT level. The functional employed is the Becke three-parameter (B3LYP) hybrid functional[22,23] which has been widely used in theoretical studies of pyrrole macrocycles.[24–28] For this purpose, the 6-31G** basis set was selected. In order to



**1**

**2a**

**2b**

**2c**

**3**

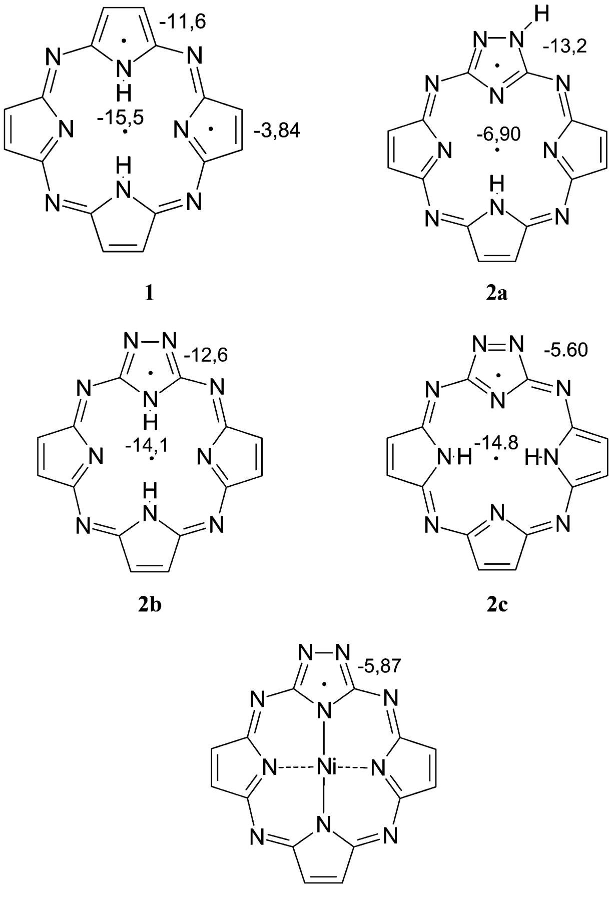
**Fig. 1** Bond lengths (Å) and bond angles (degrees) of **1**, **2a**, **2b**, **2c**, and **3** structures optimized at the B3LYP/6-31G** level.

verify that the optimized structures correspond to a minimum, they were fully characterized by vibrational analysis using second derivatives. Positive frequencies and eigenvalues of the Hessian were obtained in every case. The present work was computationally supported by the Gaussian 98 package.[29]

## 3 Results and discussion

### Geometries and energies

The present calculations predict planar structures of $D_{2h}$, $C_{2v}$, and $C_s$ symmetries for compounds **1**, **2b** and **2c**, and **2a**, respectively. In Fig. 1, the bond lengths and the angles of **1**, **2a**, **2b**, **2c** and **3** are shown while Table 1 collects some of the energies and dipole moments.



**1**

**2a**

**2b**

**2c**

**3**

**Fig. 2** Calculated NICS values (ppm) of the studied compounds.

**Table 1** Total ($E$) and relative ($\Delta E$) energies, and dipole moments ($\mu$) of structures **1**, **2a**, **2b**, **2c** and **3** optimized at the B3LYP/6-31G** level

| Structure | $E$/a.u. | $\Delta E$/kcal mol$^{-1}$ | $\mu$/Debye |
|---|---|---|---|
| **1** | −1053.72663830 | — | 0.00 |
| **2a** | −1085.75771329 | 12.54 | 2.66 |
| **2b** | −1085.77012851 | 4.75 | 7.21 |
| **2c** | −1085.77770003 | 0.00 | 6.13 |
| **3** | −2592.86816070 | — | 6.67 |

The comparison of the calculated energies for **2a**, **2b** and **2c** shows the stability increases in the order **2a** < **2b** < **2c**. From this result, one could expect **2c** to be the most abundant compound in a mixture of the tautomers. On the other hand, all triazole-porphyrazine structures show a pronounced dipole moment (see Table 1) in comparison with porphyrazine (whose dipole moment is null) as a consequence of the symmetry decrease induced by the triazole ring. Thus, this kind of planar, aromatic and noncentrosymmetrical compound with a permanent dipole moment is a putative monomer for building supramolecular organized systems with potential applications in optoelectronics and other related fields.

The proton migration in compounds **2a**, **2b** and **2c** induces significant geometry changes as can be seen in Fig. 1. The N–N bond length at the triazole ring decreases in the order **2a** > **2b** > **3** > **2c**. Compound **3** shows a value which is between those of **2b** and **2c**. This may be due to the substitution of both hydrogen atoms (present in **2b** and **2c**) by a metal (characteristic of **3**) in the macrocycle cavity. The lengths of the N–C bond (linking the N–N groups with the inner macrocycle) increase in the sequence **2a** < **2b** < **3** < **2c**, indicating that in this series the interaction between the N–N fragment and the rest of the system becomes weaker. This result is in agreement with a similar

**Table 2** EN, GEO and HOMA indices for **1**, **2a**, **2b**, **2c** and **3** structures optimized at the B3LYP/6-31G** level[a]

| Structure | EN | GEO | HOMA |
|---|---|---|---|
| **1 (whole system)** | **0.115** | **0.322** | **0.563** |
| *internal cross* | *0.022* | *0.036* | *0.942* |
| [18]heteroannulene | 0.048 | 0.185 | 0.767 |
| **2a (whole system)** | **0.122** | **0.464** | **0.414** |
| triazole ring (a) | 0.044 | 0.034 | 0.922 |
| *internal cross* | *0.015* | *0.094* | *0.891* |
| [18]heteroannulene | 0.043 | 0.243 | 0.714 |
| **2b (whole system)** | **0.103** | **0.322** | **0.575** |
| triazole ring (a) | 0.081 | 0.032 | 0.887 |
| *internal cross* | *0.018* | *0.039* | *0.943* |
| [18]heteroannulene | 0.040 | 0.157 | 0.803 |
| **2c (whole system)** | **0.098** | **0.287** | **0.615** |
| triazole ring (a) | 0.118 | 0.225 | 0.657 |
| *internal cross* | *0.016* | *0.036* | *0.948* |
| [18]heteroannulene | 0.043 | 0.203 | 0.753 |
| **3 (whole system)** | **0.080** | **0.277** | **0.643** |
| triazole ring (a) | 0.090 | 0.074 | 0.836 |
| *internal cross* | *0.019* | *0.069* | *0.912* |
| [18]heteroannulene | 0.037 | 0.207 | 0.756 |

[a] The calculated EN, GEO, HOMA and NICS for the free base porphyrin are, respectively, 0.107, 0.240, 0.666 and −16.5 ppm.[11,12]

study performed at the semiempirical level on triazolehemiporphyrazine.[30]

### The aromaticity of the triazoleporphyrazine macrocycle

Table 2 and Fig. 2 show the calculated values for the HOMA (and its components EN and GEO) and NICS indices, respectively, in the studied compounds. The data shown in Table 2 indicate that the HOMA index increases in the sequence **2a** < **2b** < **2c**. This result is in complete agreement with the NICS calculation which becomes more negative in the same sequence of compounds (Fig. 2). Accordingly, it can be concluded that the aromaticity of the triazoleporphyrazine is strongly affected by the tautomerism arising through the hydrogen migration. The aromaticity increases in the sequence **2a** < **2b** < **2c**. The tautomers **2b** and **2c** are clearly aromatic and have HOMA and NICS indices which are similar to those obtained for the free base porphyrin.[11–12] In contrast, tautomer **2a** is markedly less aromatic than the other two tautomers. A similar picture was obtained by Furuta *et al.*[15] for multiple N-confused porphyrin tautomers when one of the H atoms was bonded to the "external" N of the confused pyrrole group. Their calculated NICS values for the singly N-confused porphyrin were −13.8 and −7.7 ppm, for tautomers $N_1CP_2$ and $N_1CP_4$, respectively. These tautomers are homologues of compounds **2c** and **2a**, respectively.

The increase of the aromaticity correlates very well, as expected from the classical energetic comprehension of this concept, with the stability of the considered tautomers.

The substitution of the tautomerism-determining H atoms by a metal atom (Ni in our study) which is placed at the center of the macrocycle cavity increases the aromaticity of the triazoleporphyrazine macrocycle. This is proved by the increase of the HOMA index (see Table 2). This result is consistent with the spectroscopic UV-visible data for the corresponding peripherally substituted derivatives obtained in experimental studies.[9] Also it is in agreement with the calculations of Cyranski *et al.*[12] who found the HOMA increased up to 0.671 for the porphyrin metal complex.

The *internal cross* is the most aromatic part of structures **2b**, **2c** and **3** (also in structure **1**). This feature is also exhibited by porphyrins.[11,12] The calculated HOMA indices are 0.943, 0.948 and 0.912 for **2b**, **2c** and **3**, respectively and are similar to the value (0.932) previously reported for the porphyrin.[11,12] The HOMA of the *internal cross* in compound **2a** is only a little smaller than that in the triazole ring (despite the fact that this result is formally in contradiction with Huckel's rule since **2a** has 17 electrons). Consequently, it can be considered that this case reinforces the described general situation. This, in turn, indicates that in order to form an aromatic macrosystem from the heterocycles which are similar to those present in porphyrins, their aromaticity should be decreased or lost.

It is interesting to note that the aromaticity of the *internal cross* in the Ni-substituted derivative (**3**) is lower than that corresponding to compounds **2b** and **2c**. This situation has been also described for the porphyrin and its metal complex.[11,12] It seems that the electron shift from the ligand to the metal affects negatively the aromaticity of the macrocycle. In fact, the mean $p_z$ occupancy of the 16-member *internal cross* (using NBO calculation) decreases from 1.11 in compounds **2b** and **2c** to 1.08 in compound **3**.

In a coarser approximation, the HOMA of the [18]heteroannulene fragments of compounds **1**, **2b**, **2c** and **3** are very similar (see Table 2), indicating their structural similarity. As in the case of the *internal cross*, the HOMA value of the [18]-heteroannulene sub-unit in tautomer **2a** does not significantly differ from the values corresponding to the other compounds. This occurs even though a formal construction of this contour following the sequence of double/single bonds seems to be broken in the triazole ring. A more careful analysis can distinguish tautomer **2b**, with the highest HOMA value (see Table 2), as the only 18-member fragment that includes the N–N bond of the triazole ring. Compounds **1**, **2c** and **3** having [18]heteroannulenes with the same composition have the most similar HOMA values among those shown by the complete series of considered structures. One of the conclusions that can be drawn is that the incorporation of the N–N bond of the triazole ring increases the structural aromatic character of the [18]heteroannulene ring of **2b**.

The relatively high values of the HOMA index for the *internal cross* and [18]heteroannulene sub-units in tautomer **2a** seem to be in open contradiction with the low values of the aromaticity indices for the whole molecule. Nevertheless, this situation consolidates the idea that this phenomenon is profoundly complex and, consequently, is difficult to afford it with an unilateral approach.

A similar situation to that discussed above is observed when analyzing the aromatic character of the triazole ring. In structure **2a**, the local aromaticity indices are the highest obtained for this family of compounds (see Table 2 and Fig. 2) and are similar to those of the free 1,2,4-triazole.[11,12] Thus, the triazole moiety retains its aromaticity when it is incorporated into the nonaromatic (or less aromatic) macrocycle **2a**. The high aromaticity indices of the triazole ring for the **2a** tautomer are in correspondence with the fact that the N–N bond has a very pronounced double character as was previously pointed out (see the above section). However, for structures **2b**, **2c** and **3**, the triazole ring is involved in the aromatic macrosystem and decreases its local aromaticity. The NICS indices indicate that the aromaticity of the triazole ring differs significantly in **2b** with respect to **2c**. This difference may be understood taking into account the contribution of the H bonded to the pyrrole nitrogen as is observed in compound **1**.

It is evident that the presence of an H atom in position 1 of the triazole ring in tautomer **2a** provokes a sensible decrease of the overall aromaticity but preserves its structural sub-spaces with large conjugation. This conclusion may be important for the design of molecular macrosystems with desired electronic properties.

The behavior of compound **1** in the series of free-base systems studied in the present work reveals that the expected correlation of the whole HOMA with the NICS is valid for **2a**, **2b** and **2c** but not for **1**. This result is related to the different nature of each system.

The HOMA is a geometry-based criterion and, consequently, is more sensitive to geometry changes. In compounds **2**, the incorporation of the N–N bonds of the triazole ring increases the structural aromatic character of the tautomers **2b** and **2c** with respect to compound **1** when the aromaticity is described in terms of the HOMA. Thus, the N–N bond length in compounds **2** (1.309 Å for **2b** and 1.279 Å for **2c**) is shorter than the C–C bond distance for the β carbons of the pyrrole groups in compound **1** (1.366 Å). This fact gives rise to a compression of the system of alternated double/simple bonds. The present analysis is fully applicable to the comparison, for example, of the HOMA values for the [18]heteroannulene sub-units of compounds **1** and **2b**.

On the other hand, the NICS calculation, based on the magnetic properties of the π electron systems, indicates that compound **1** is more aromatic than compounds **2** due to the presence of more nitrogen atoms in the conjugated sequence of the latter. In fact, the increment of the electronegativity of one of the members of the conjugated system may limit the electronic delocalization within the ring. This situation is rationally explained using the definition of the NICS if one considers that the induced electronic current within the ring (due to the π electron movement induced by an external magnetic field) is less intense because the additional resistance that appears when a less electronegative carbon atom is substituted by a more electronegative nitrogen atom. This explanation can also be applied to discern why the calculations for the porphyrazine (compound **1**) and the triazoleporphyrazine (compounds **2**) indicate that these compounds are less aromatic than the porphyrin (see Table 2). The NBO calculations yield extreme $p_z$ electronic occupancies at the *meso* atoms of 1.021 and 1.187 for the porphyrin and **2a**, respectively, and intermediate values (from 1.163 to 1.180) for **1**, **2b**, **2c** and **3**.

The two previous analyses have limited character, thus they are related to either a specific structure or a typical property of the compounds. Nonetheless, we must emphasize the loss of the correlation is related to compound **1** which, in turn, is the one showing a different composition. In our opinion this indicates that aromaticity studies based on quantitative criteria have to be carefully done and that definitive conclusions should be avoid when the analyzed systems are not compositionally and structurally homogeneous.

## 4 Conclusions

The tautomerism in the free-base triazoleporphyrazine induces significant changes in the geometry and electronic properties of the macrocycle. Tautomers in which both H atoms point into the macrocycle cavity (**2b** and **2c**) are planar structures with multicontour conjugated macrosystems bearing 18 π-electrons and, consequently, are aromatic. In contrast, structure **2a**, which preserves the planarity of the macrocycle but has one of the H atoms in the position 1 of the triazole ring, is less aromatic. This does not prevent the other structural fragments in this tautomer, such as the triazole ring, the *internal cross* and the [18]heteroannulene, exhibiting large aromatic character, despite their weak conjugation with the rest of the macrocycle. In summary, structures **2a**, **2b**, and **2c** are the first examples of porphyrazine-like molecules in which the conjugation over the macrocycle is limited by tautomerization.

The *internal cross* of the triazoleporphyrazine tautomers is the most aromatic part of these structures. The aromatic character of the triazoleporphyrazine macrocycle as a whole is increased by the substitution of the H atoms by a metal atom in the centre of the macrocycle cavity. This structural change reduces simultaneously the conjugation of the *internal cross*.

A high correlation was observed (as corresponds to the energetic approach of the aromaticity) between the aromaticity HOMA and NICS indices and the total electronic energy of the optimised structures **2a**, **2b**, and **2c**.

The comparative analysis of the aromaticity in porphyrin, porphyrazine and triazoleporphyrazines strongly supports the proposal that aromaticity studies based on quantitative criteria have to be carefully done and that definitive and generalizing conclusions should be avoided when the considered systems are not compositionally and structurally homogeneous.

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