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PAPER

The origin of global and macrocyclic aromaticity in porphyrinoids

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The global and macrocyclic aromaticity of porphyrinoids was characterized using our graph theory of aromaticity. The sequential line plots of topological resonance energy (TRE) against the number of π-electrons (N_π) for different porphyrinoids are similar with four major extrema to those for five-membered heterocycles. This supports the view that five-membered rings are the main origin of global aromaticity in porphyrinoids. Macrocyclic circuits contribute significantly to macrocyclic π-circulation but modestly to global aromaticity. Macrocyclic aromaticity/antiaromaticity in oligopyrrolic macrocycles can be predicted by formally applying Hückel's [4*n* + 2] rule to an annulene-like main macrocyclic conjugation pathway (MMCP). This bridged annulene model can be justified by examining the contribution of individual macrocyclic circuits to macrocyclic aromaticity. A Hückel-like rule of macrocyclic aromaticity was found for porphyrinoid species.

1. Introduction

During the past three decades, various kinds of porphyrinoids have been prepared and characterized. Most porphyrin chemists have been interested in macrocyclic aromaticity but not in global aromaticity.[1–12] Macrocyclic aromaticity is associated with macrocyclic circuits and global one with all circuits.[13–18] In this study, circuits indicate all possible cyclic or closed paths in a cyclic π-system. Macrocyclic circuits are cyclic paths that enclose the inner cavity. Proton chemical shifts, macrocyclic π-circulation and kinetic stability are determined primarily by macrocyclic aromaticity. Hückel's [4*n* + 2] rule of aromaticity[19,20] has been applied formally to the main macrocyclic conjugation pathway (MMCP) in porphyrinoids to predict the macrocyclic aromaticity/antiaromaticity.[1–12] Here, an MMCP is an annulene-like macrocyclic circuit consisting of alternating single and double bonds. Recently, we pointed out that most porphyrinoid species exhibit global aromaticity with positive topological resonance energies (TREs).[13–18]

Polycyclic benzenoid hydrocarbons, usually referred to as polycyclic aromatic hydrocarbons (PAHs), are benchmark molecules in aromatic chemistry.[21,22] Hückel's original [4*n* + 2] rule, however, is known to be inapplicable to polycyclic π-systems.[23] We found that a variety of PAHs resemble each other in the dependence of TRE on the number of π-electrons (N_π), where N_π runs from 0 to twice the number of conjugated atoms ($2N_{ca}$).[24] A similar aspect of global aromaticity was observed for different groups of polycyclic π-systems formed by fusion of two or more rings of the same size.[24] Such a dependence of TRE on N_π, instead of Hückel's [4*n* + 2] rule, might possibly serve as a useful tool for aromatic chemistry. In this paper, we apply this kind of graph-theoretical methodology to various porphyrinoid species and explore the main origin of global and macrocyclic aromaticity in conjunction with their molecular geometry. The bridged annulene model for free-base porphyrins (*i.e.*, oligopyrrolic macrocycles)[1–12] is then justified by analyzing the contribution of individual macrocyclic circuits to macrocyclic aromaticity and π-circulation.

2. Theory and computational methods

Among the attractive topics in the chemistry of porphyrinoids is aromaticity. In traditional chemistry,[20,23,25] the term 'aromaticity' describes molecules that benefit energetically from the delocalization of π-electrons in closed circuits. The TRE concept has been used as an energetic criterion of aromaticity for a variety of neutral and charged cyclic π-systems.[23,26,27] It is a kind of aromatic stabilization energy (ASE), defined as a difference in total π-electron energy between a given cyclic π-system and the graph-theoretically defined polyene reference.[23,26,27] Positive and negative TREs indicate aromaticity and antiaromaticity, respectively.

Bond resonance energy (BRE) is defined as follows.[28–30] A hypothetical π-system, in which a given π-bond (*e.g.*, a π-bond formed between the *p*th and the *q*th atoms) interrupts cyclic conjugation thereat, can be constructed by multiplying $\beta_{p,q}$ by i and $\beta_{q,p}$ by $-i$, where $\beta_{p,q}$ and $\beta_{q,p}$ are the resonance integral between the two conjugated atoms and i is the square root of -1. In this π-system, no circulation of π-electrons occurs along the circuits that share the $p - q$ π-bond. BRE for the $p - q$ π-bond is given as a destabilization energy of this hypothetical π-system. In other words, BRE represents the contribution of all

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circuits that pass through the π-bond to TRE.[28–30] This quantity was originally introduced to justify the isolated pentagon rule for fullerenes.[28] If the minimum BRE in a molecule (min BRE) is smaller than $-0.100\ |\beta|$, it is highly probable that the molecule will be kinetically very unstable.[28–30]

Superaromatic stabilization energy (SSE) represents the extent of macrocyclic aromaticity,[15,17] which constitutes part of TRE for an entire π-system. For all porphyrinoids, SSE is identical to the BRE calculated for any of the π-bonds that link pyrrolic and/or other small rings circularly.[13] BREs for all such π-bonds in a porphyrinoid molecule are the same in magnitude. We hereafter use the term 'macrocyclic aromaticity' as a synonym of the terms 'superaromaticity' and 'porphyrinoid aromaticity'.

According to our graph-theoretical variant[31,32] of the Hückel-London theory of ring-current diamagnetism,[33] a π-current induced in a polycyclic π-system G is given as a superposition of π-currents induced separately in individual circuits. The intensity of a π-current induced in the ith circuit, I_i, is proportional not only to the area of the circuit but also to the quantity defined by:[31,32]

$$A_i = 4\prod_{p>q}^{r_i} k_{p,q} \sum_{j}^{\mathrm{occ}} \frac{P_{G-r_i}(X_j)}{P_G{}'(X_j)} \qquad (1)$$

where r_i is a set of conjugated atoms that form the ith circuit; $k_{p,q}$ is the resonance integral parameter for a π-bond located along the ith circuit; $p > q$ runs over all π-bonds that belong to the circuit; $G - r_i$ is the subsystem of G, obtained by deleting r_i from G; $P_G(X)$ and $P_{G-r_i}(X)$ are the characteristic polynomials for G and $G - r_i$, respectively; X_j is the jth largest zero of $P_G(X)$; a prime added to $P_G(X)$ indicates the first derivative with respect to X; and j runs over all occupied π molecular orbitals (πMOs). If there are degenerate πMOs in G, eqn (1) must be replaced by others.[31,34] Then, I_i is expressed exactly in the form:[31,32]

$$I_i = 4.5 I_0 A_i \frac{S_i}{S_0} \qquad (2)$$

where S_i and S_0 are the areas of the ith circuit and the benzene ring, respectively, and I_0 is the intensity of the ring current induced in the benzene ring under the same experimental conditions. Thus, I_i is given in units of the benzene value.

On the basis of our previous discussion on ring-current diamagnetism,[35,36] the A_i value can be interpreted as an ASE arising from cyclic π-conjugation in the ith circuit. To be more exact, it is an ASE-like quantity derived from the magnetic response of the π-system.[35,36] This quantity was termed as circuit resonance energy (CRE) for the circuit concerned. In fact, the sum of CREs over all macrocyclic circuits is close to SSE,[35–38] so that we can estimate from the CREs the relative contributions of individual circuits to global and macrocyclic aromaticity. This complements the drawback of TRE that it cannot be partitioned among the circuits.

Porphyrinoids chosen in this study are presented in Fig. 1. For the sake of simplicity, all substituents and possible deviation of a porphyrinoid π-system from planarity are disregarded. All these porphyrinoid π-systems are assumed to be in a singlet electronic state. Van-Catledge's Hückel parameters for heteroatoms[39] are used. Nitrogen atoms coordinated to metal ions are dealt with as imine nitrogens.[13] Realistic molecular geometry is necessary to evaluate the intensities of circuit currents. We used the molecular geometry of free-base porphine (**1**) calculated by Jusélius and Sundholm[40] at the resolution-of-the-identity density-functional theory (RI-DFT) level[41] using the Becke–Perdew (B–P) parametrization[42–44] as implemented in TURBOMOLE[45] and the geometry of orangarin (**9**) calculated by us at the B3LYP/6-31G** level of theory using the Gaussian 03 suite of programs.[18,46] All non-identical circuits in **1** and **9** are shown in Fig. 2.

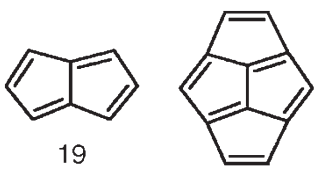
3. Results and discussion

Among the porphyrinoids studied are free-base porphyrins (**1**, **3**, **9**, **10**, **15** and **16**), metalloporphyrins (**2** and **18**), fused porphyrins (**13**, **14**, **17** and **18**), confused porphyrins (**4**, **5** and **11–14**), expanded porphyrins (**9–12** and **15–18**), Möbius-twisted porphyrins (**16** and **18**) and porphyrinoids with non-pyrrolic rings (**6–8**). Confused porphyrin **4** is a valence tautomer of **1**. Two doubly N-confused porphyrins **11** and **12** are different in the oxidation level.[47] General properties of **1–18** are described in ref. 1–17 and 47 and so are not repeated here. The π-networks of **2** and **18** are negatively charged, but all species including these two will be dealt with as neutral species since the entire molecules have no net charge.

Global aromaticity of porphyrinoids

We first make a general survey of the global aromaticity of porphyrinoids. TREs for **1–18** are listed in Table 1. All these species are moderately aromatic with positive TREs.[13–18] No globally antiaromatic porphyrinoids have been synthesized yet. TREs for **1–18** are shown graphically in Fig. 3 as sequential line plots (*i.e.*, the sequential line graphs) of TRE against N_π, where arrows point to the neutral species. Each plot represents the N_π dependence of global aromaticity, where N_π necessarily corresponds to the neutral or charged species with N_π π-electrons. Within the Hückel framework, N_π varies in the 0 to $2N_{ca}$ range.

It is noteworthy that the 18 line plots in Fig. 3 are very similar in appearance to each other. All plots have four major extrema in common (*i.e.*, two maxima and two minima); these maxima and minima correspond to hypothetical molecular ions with maximum and minimum TREs, respectively. Such a variation of TRE is a notable characteristic of polycyclic conjugated hydrocarbons formed by fusion of two or more five-membered rings,[24] such as pentalene (**19**) and dicyclopenta[*cd*,*gh*]pentalene (**20**).[48] Therefore, we can presume that the main origin of global aromaticity in **1–18** and their molecular ions might be local five-site circuits, such as **1a** and **1b** of free-base porphine (**1**) and **9a**, **9b** and **9c** of orangarin (**9**) in Fig. 2. This finding strongly suggests that macrocyclic circuits do not contribute significantly to global aromaticity although the number of such circuits is large. For all species but *m*-benziporphyrin (**7**), the molecular cation with $N_\pi = N_{ca}$ is almost non-aromatic with a very small negative or positive TRE.



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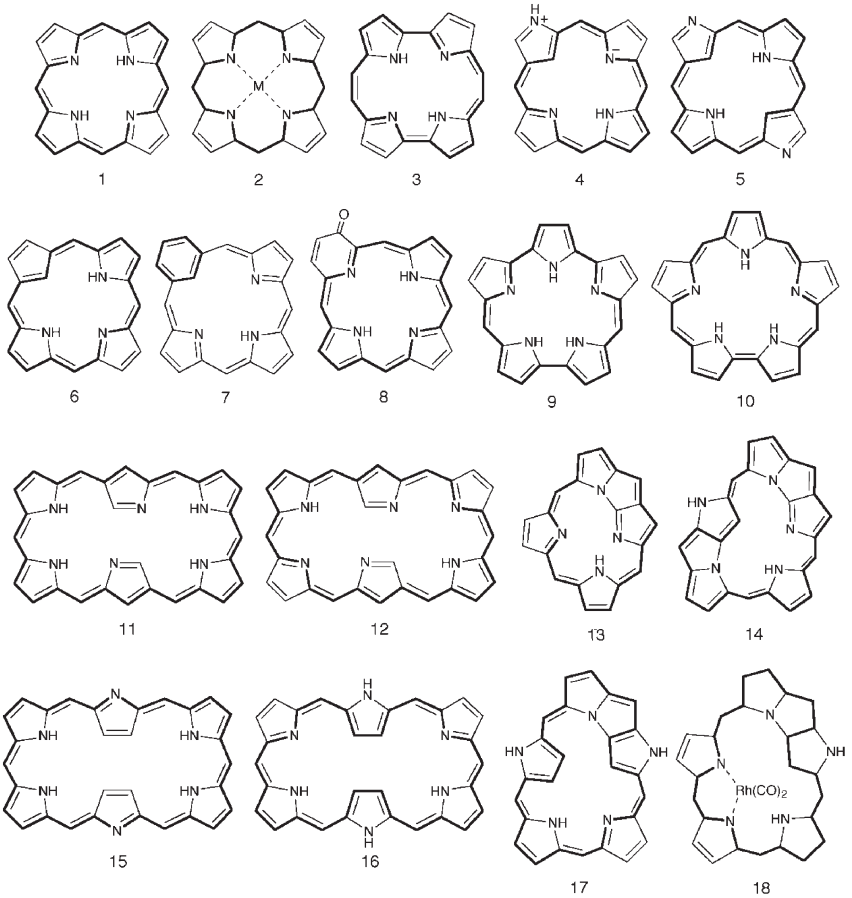
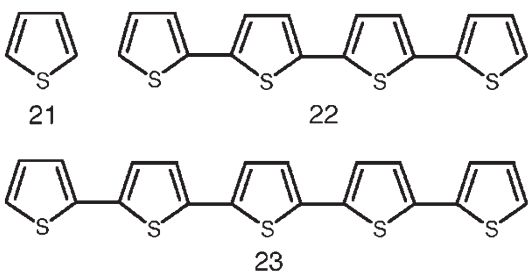


Fig. 1 Twenty porphyrinoids studied. Species **16** and **18** have Möbius-twisted macrocycles.

In order to confirm the above reasoning on global aromaticity, we examined the N_π dependence of TRE for non-macrocyclic heterocycles, thiophene (**21**), α-quaterthiophene (**22**) and α-quinquethiophenes (**23**).[49,50] Unlike **19** and **20**, five-membered rings in **22** and **23** are not fused to each other. TREs for these molecules are listed in Table 2. Line plots of TRE against N_π for **21**–**23** are shown in Fig. 4. These molecules are devoid of macrocyclic aromaticity but still highly aromatic with positive TREs when they have six π-electrons per ring. The TRE *vs.* N_π plots for these species are again similar in shape not only to each other but also to those for many porphyrinoids. All these plots have four prominent extrema, two maxima and two minima; the molecular polycation with $N_\pi = N_{ca}$ is almost non-aromatic with a very small negative or positive TRE. These common features of the plots further support the above view that the main origin of global aromaticity in many porphyrinoids must be individual five-membered rings. The macrocyclic structure in porphyrinoids hardly affects the gross shape of the TRE *vs.* N_π plots.



Among the porphyrinoids studied, *m*-benziporphyrin (**7**) and oxypyriporphyrin (**8**) contain one six-membered ring in place of one of the usual pyrrolic units. Close examination of Fig. 3 revealed that the TRE *vs.* N_π plots for these two species are slightly different in fine structure from those for porphyrinoids containing only five-membered rings. Molecular cation of **7** with $N_\pi = N_{ca}$ is aromatic with a positive TRE. TREs for unrealistic molecular anions of **7** and **8** with $N_\pi = 2N_{ca} - 2$ are marked with asterisks. These polyanions have small positive TREs, which are in contrast to those of other porphyrinoids with small negative TREs. Such local anomalies in the TRE *vs.* N_π plots must reflect the presence of six-membered rings,[24] suggesting that six-site circuits are small enough to create appreciable local structures in the plots. For reference, the TRE *vs.* N_π plot for benzene (**24**) is shown in Fig. 5, in which the polyanion with $N_\pi = 2N_{ca} - 2$ (namely, 10 π-electrons) has a positive TRE. Oxypyriporphyrin (**8**) has an oxypyri subunit, a kind of six-membered ring. This ring, however, does not seem to be aromatic in the neutral species because of its quinonoid structure. As expected from many other porphyrinoids, the molecular dication of **8** with $N_\pi = N_{ca}$ is almost non-aromatic. If the number of constituent six-membered rings increases in the porphyrinoid π-system, the TRE *vs.* N_π plot will resemble that for **24** more closely.

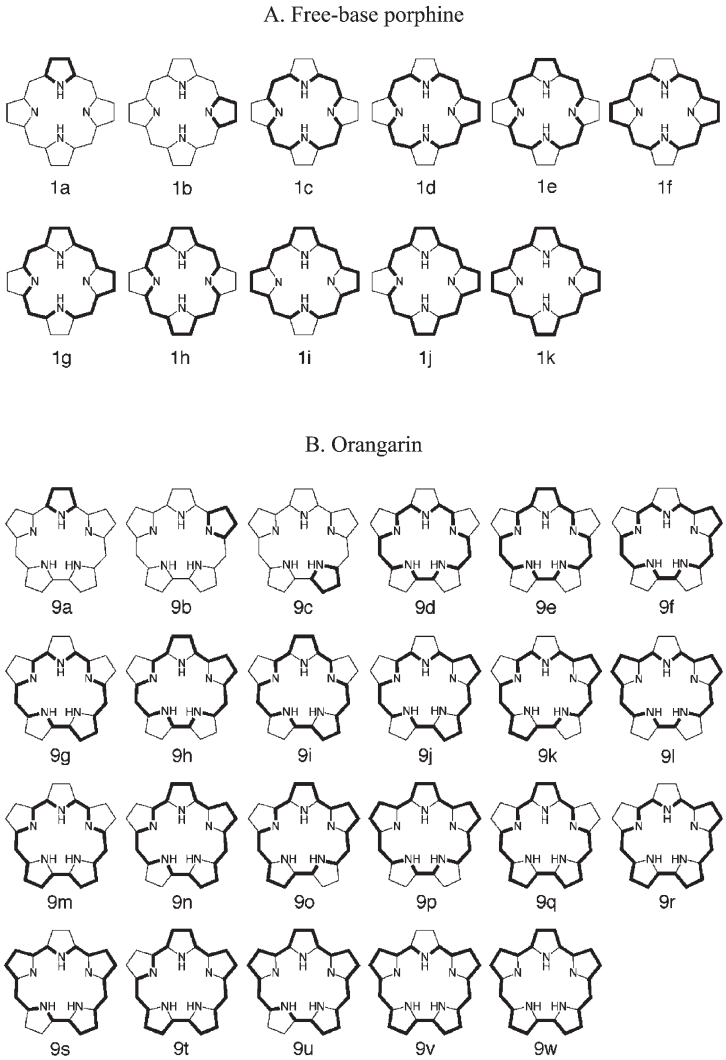


Fig. 2 Non-identical circuits in free-base porphine (**1**) and orangarin (**9**).

Application of the extended Hückel rule

Hückel's [4*n* + 2] rule of aromaticity cannot be applied to porphyrinoids because they have polycyclic π-systems.[23] The extended Hückel rule proposed by Hosoya *et al*.[51–53] can instead be applied to circuits in polycyclic π-systems. According to this rule and the concept of a conjugated circuit proposed by Herndon[54] and Randić,[55] small conjugated circuits are the main source of aromaticity in neutral polycyclic conjugated hydrocarbons. This idea may not be naïvely applicable to charged π-systems nor to heterocycles, but smaller circuits are still likely to contribute significantly to the global aromaticity/antiaromaticity of these π-systems, because they contribute much to the coefficients of the characteristic polynomial.[51] Macrocyclic circuits in porphyrinoids are very large compared to local five-site circuits, so that they must contribute modestly not only to TRE but also to the TRE *vs.* N_π plot.

When a porphyrinoid molecule gradually gains or loses π-electrons to form different molecular ions, the average number of π-electrons residing on individual pyrrolic five-site circuits varies from *ca.* 6 to 10 or from *ca.* 6 to 0. Accordingly, five-site circuits must oscillate between aromaticity and antiaromaticity, depending on the average number of π-electrons they carry. The entire π-system must likewise oscillate between aromaticity and antiaromaticity. This must be why four major extrema appear in the TRE *vs.* N_π plots for porphyrinoids.

Macrocyclic aromaticity of porphyrinoids

In our theoretical treatment,[13,15] SSE represents the extent of macrocyclic aromaticity; positive and negative SSEs indicate macrocyclic aromaticity and antiaromaticity, respectively. SSEs for **1–18** are listed in Table 3, together with those for their divalent molecular ions. Among the porphyrinoids studied, those but **9**, **11**, **14**, **15** and **17** have positive SSEs. These species are globally aromatic and macrocyclically aromatic (*i.e.*, superaromatic) species. By contrast, **9**, **11**, **14**, **15** and **17** have negative SSEs. These porphyrinoids are globally aromatic with positive TREs but macrocyclically antiaromatic (*i.e.*, superantiaromatic) with negative SSEs. For all porphyrinoids, SSE is much smaller than TRE. Therefore, it is numerically true that macrocyclic

Table 1 TREs and SSEs for twenty porphyrinoids

Species	Trivial name[a]	Number of π-electrons[b]	TRE/|β|	SSE/|β|	(TRE-SSE)/|β|
1	Free-base porphine	26 (18)	0.4322	0.0843	0.3499
2	Metal(II) complex of porphyrin	26 (18)	0.4744	0.0795	0.3949
3	Porphycene	26 (18)	0.4862	0.0779	0.4083
4	N-confused porphyrin	26 (18)	0.4394	0.0501	0.3893
5	Doubly N-confused porphyrin	26 (18)	0.3812	0.0660	0.3152
6	Carbaporphyrin	26 (18)	0.3820	0.0760	0.3060
7	*m*-Benziporphyrin	26 (–)	0.3866	0.0085	0.3781
8	Oxypyriporphyrin	28 (18)	0.4232	0.0750	0.3482
9	Orangarin	30 (20)	0.5656	−0.0696	0.6352
10	Sapphyrin	32 (22)	0.5904	0.0639	0.5265
11	Doubly N-confused [28]hexaphyrin	40 (28)	0.5992	−0.0379	0.6371
12	Doubly N-confused [26]hexaphyrin	38 (26)	0.4422	0.0401	0.4021
13	N-fused porphyrin	26 (18)	0.2988	0.0407	0.2581
14	Doubly N-fused pentaphyrin	34 (24)	0.4870	−0.0466	0.5336
15	[28]hexaphyrin	40 (28)	0.5371	−0.0955	0.6326
16	Möbius-twisted [28]hexaphyrin	40 (28)	0.6743	0.0547	0.6196
17	N-fused pentaphyrin	34 (24)	0.4364	−0.1410	0.5774
18	Möbius-twisted Rh(I) complex of N-fused pentaphyrin	34 (24)	0.6732	0.0605	0.6127

[a] Some of these names may be imprecise ones. [b] Values in parentheses indicate the nominal number of π-electrons located along the main macrocyclic conjugation pathway (MMCP).

conjugation is never the main origin of global aromaticity. N-fused pentaphyrin (**17**) has been synthesized although the SSE is less than −0.100 |β|; macrocyclic antiaromaticity must be greatly diminished by deforming the π-system.[56]

Local aromaticity of porphyrinoids

For porphyrinoids, global aromaticity consists of two parts: macrocyclic aromaticity and local aromaticity. Local aromaticity arises from small constituent rings. As SSE is an ASE arising from all macrocyclic circuits, the difference between TRE and SSE can be attributed to local aromaticity. SSEs for 18 porphyrinoids, together with the differences between TRE and SSE, are added in Table 1. The fact that the TRE-SSE difference is much larger than SSE is fully consistent with the predominant contribution of local rings to global aromaticity.

Sessler *et al.* explicitly stated that cross-conjugated porphyrinoids, such as cyclo[*m*]pyridine[*n*]pyrroles[57] and dihydroimidacene,[58] are best described as locally aromatic compounds devoid of long-range intersubunit conjugation. It is indeed true that many cross-conjugated porphyrinoids, including benziporphyrin (**7**), have high local aromaticity but has little macrocyclic aromaticity. At the same time, one should note that all porphyrinoids so far prepared have local aromaticity whether or not they exhibit macrocyclic aromaticity/antiaromaticity. Five- and six-membered rings incorporated in porphyrinoids are aromatic in nature. In principle, all circuits in a π-system contribute more or less to aromatic or antiaromatic character.[26,27,51–53]

Orangarin (**9**) is what has been called a typical 'antiaromatic' porphyrin. As reported by Sessler *et al.*,[59,60] the macrocycle of **9** is antiaromatic with a negative SSE of −0.0696 |β|. However, the TRE-SSE difference is as large as 0.6352 |β|, which indicates that five constituent pyrrolic rings in **9** are still the origin of high local aromaticity. In our terminology, this molecule is a macrocyclically antiaromatic (*i.e.*, superantiaromatic) but locally aromatic species. Porphyrinoids **9**, **11**, **14**, **15** and **17** likewise have been classified as 'antiaromatic species'. They also are macrocyclically antiaromatic but locally aromatic porphyrinoids. According to Sargent *et al.*,[58] the molecular dianion of porphycene ($\mathbf{4}^{2-}$) has an antiaromatic macrocyle but the five pyrrolic rings in it are aromatic. As summarized in Table 4, the NICS (nucleus-independent chemical shift)[61] value at the center of the dianion is positive in sign, whereas those at the centers of the pyrrolic rings are all negative.[58] Thus, there is no doubt that macrocyclic antiaromaticity concurs with local aromaticity.

The bridged annulene model

Porphyrin chemists usually attribute macrocyclic aromaticity/antiaromaticity to the main macrocyclic conjugation pathway (MMCP).[1–12] This picture of porphyrinoids is called the bridged annulene model, in which the inner NH groups of pyrrole rings and the outer C_2H_2 groups of 2H-pyrrole rings are viewed as rather inert bridges. The essence of this model is that the magnetotropicity of the porphyrinoid macrocycle and the sign of SSE can be predicted correctly by formally applying Hückel's [4*n* + 2] rule to the MMCP. On the other hand, the magnetotropicity of the Möbius-twisted porphyrinoid macrocycle and the sign of SSE can be predicted by formally applying the reverse of the Hückel rule to the MMCP.[8] The [18]annulene model is one of the bridged annulene models applicable to porphyrinoids **1**, **3–6** and **8**.

We previously reported that an MMCP can be determined by choosing a π-bond with a larger BRE at every bifurcation in the porphyrinoid π system.[13,15,17] Heavy lines in Fig. 1 indicate the MMCPs determined in this manner. For example, the MMCP in **1** is identical to circuit **1h** in Fig. 2A. In the case of porphyrinoids with negative SSEs, such as orangarin (**9**), an MMCP is determined by choosing a π-bond with a smaller BRE at every bifurcation in the π system.[13,15,17] The MMCP in **9** is identical to circuit **9q** in Fig. 2B. An MMCP cannot be defined for cross-conjugated porphyrinoids, such as *m*-benziporphyrin (**7**),

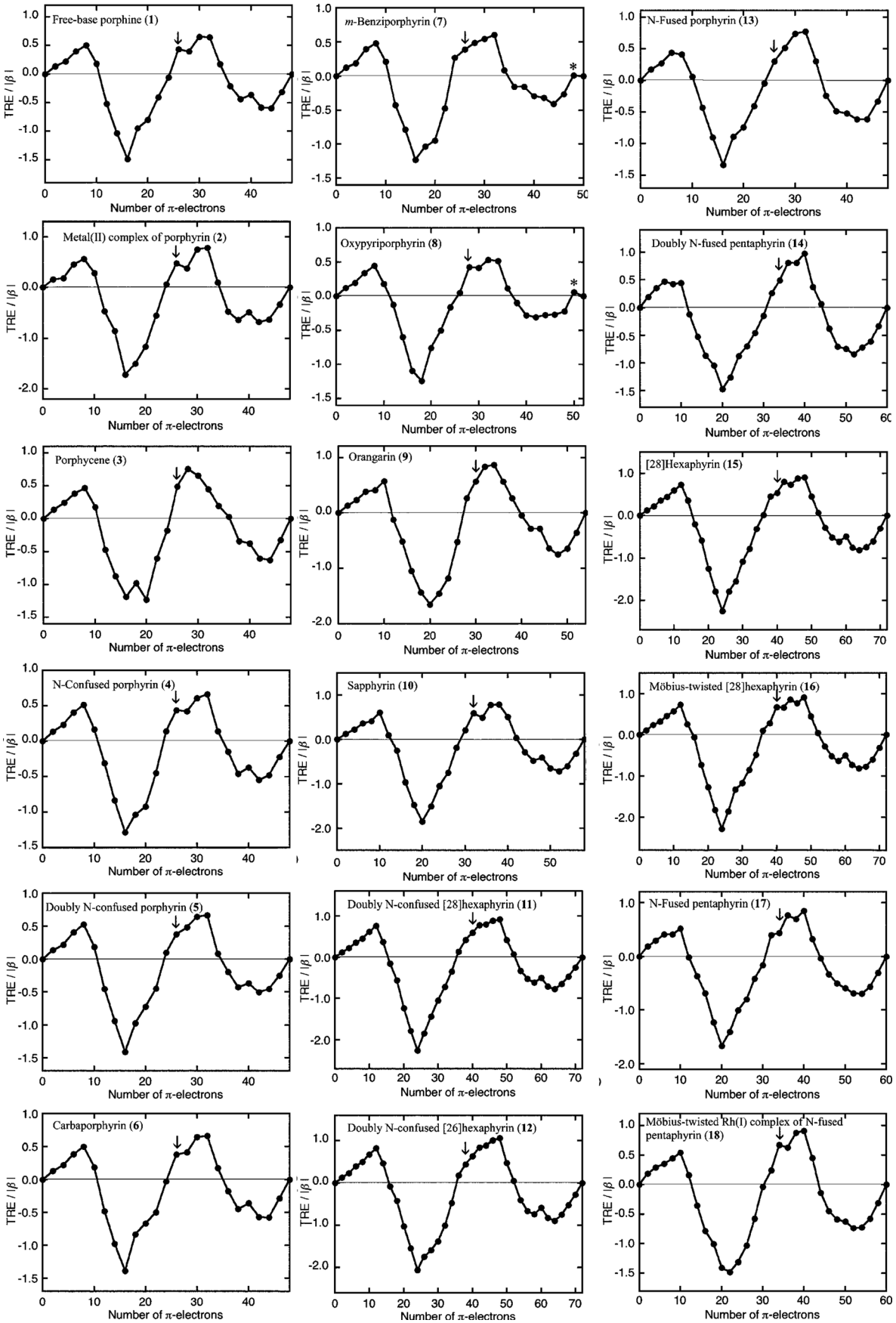
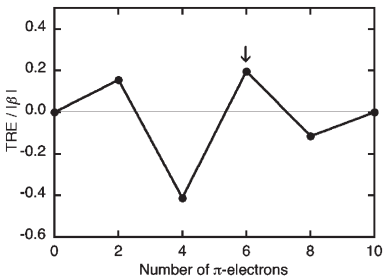


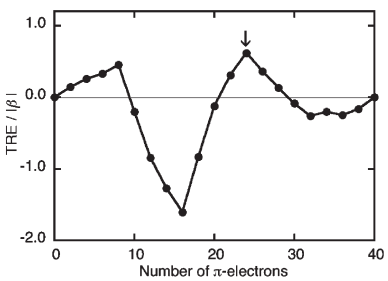
Fig. 3 TREs for 18 porphyrinoids, each as a function of the number of π-electrons (N_π). Arrows point to the neutral molecule.

Table 2 TREs for related compounds with five-membered rings

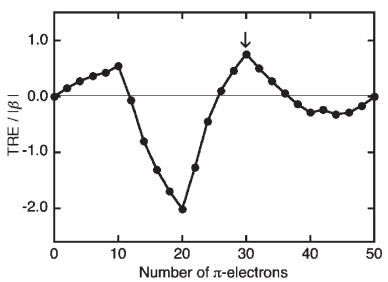
Species	Number of π-electrons	TRE/|β|
Thiophene (**21**)	6	0.1965
α-Quaterthiophene (**22**)	24	0.6167
α-Quinquethiophene (**23**)	30	0.7513



Thiophene (**21**)



α-Quaterthiophene (**22**)



α-Quinquethiophene (**23**)

Fig. 4 TREs for thiophene (**21**) and two α-oligothiophenes (**22** and **23**), each as a function of the number of π-electrons (N_π). Arrows point to the neutral molecule.

because there are no macrocyclic conjugated circuit.[55] Therefore, SSEs are supposed to be very small for these species; **7** really has a very small SSE of 0.0085 $|\beta|$, exhibiting virtually no macrocyclic aromaticity.[4,7]

Remember, however, that SSE is an ASE arising not from an MMCP alone but from all macrocyclic circuits.[13] An MMCP is only one of many macrocyclic circuits. As can be seen from Fig. 2A and Table 5A, as many as 16 macrocyclic circuits can be chosen even from relatively small free-base porphine (**1**). Much more macrocyclic circuits can be chosen from larger expanded

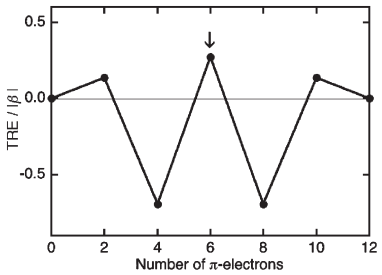


Fig. 5 TRE for benzene (**24**) as a function of the number of π-electrons (N_π). The arrow point to the neutral molecule.

porphyrins, such as **9–18**. Therefore, it is very strange that macrocyclic aromaticity/antiaromaticity can be predicted by applying Hückel's [4*n* + 2] rule to the annulene-like MMCP alone.[1–12]

Justification for the bridged annulene model

Why is the bridged annulene model so useful and popular among porphyrin chemists? The popularity of this model never means that all macrocyclic circuits but the MMCP contribute little to macrocyclic aromaticity. We can elucidate this problem in terms of CREs. Note that the extent of macrocyclic aromaticity can be estimated not only from SSE but also from a sum of CREs for all macrocyclic circuits.[62] CREs for all non-identical circuits in free-base porphine (**1**) and orangarin (**9**) are listed in Table 5. MMCPs in **1** and **9** are **1h** in Table 5A and **9q** in Table 5B, respectively. It is clear from this table that the CRE for the MMCP never dominates the sign and magnitude of the sum of CREs for all macrocyclic circuits. As for **1**, the sum of CREs over all macrocyclic circuits but the MMCP is much larger than the CRE for the MMCP. In the case of **9**, the sum of negative CREs over all macrocyclic circuits but the MMCP is much larger in absolute value than the negative CRE for the MMCP.

We, however, found that all macrocyclic circuits (**1c–1k** in Fig. 2A and Table 5A) in the neutral molecule of **1** are aromatic with positive CREs, which is fully consistent with the positive SSE. In contrast, all macrocyclic circuits (**9d–9w** in Fig. 2B and Table 5B) in the neutral molecule of **9** are antiaromatic with negative CREs, which is again fully consistent with the negative SSE. In fact, as far as oligopyrrolic macrocycles (free-base porphyrins) are concerned, CREs for all or most macrocyclic circuits have the same sign as CRE for the MMCP. This explains qualitatively why macrocyclic aromaticity/antiaromaticity can be predicted from the nominal number of π-electrons that reside on the MMCP. Among the macrocyclic circuits in a porphyrinoid species, the MMCP exhibits the largest positive or negative CRE, because it is often the only macrocyclic conjugated circuit.[51–55]

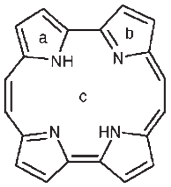
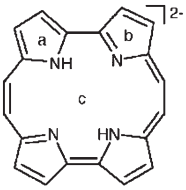
In experiments, macrocyclic aromaticity/antiaromaticity is inferred from observed proton chemical shifts. In our theory,[31,32] the ring-current distribution in a polycyclic π-system is given by superposing π-electron currents induced in all circuits. As can be seen from eqn (2), the intensity of a π-current induced in a given circuit is proportional to the CRE multiplied by the area of the circuit. Therefore, some of the macrocyclic circuits may

Table 3 SSEs for porphyrinoid molecular ions

Species	Number of π-electrons[a]	SSE/|β| Dication	Neutral	Dianion
1	26 (18)	−0.0942	0.0843	−0.1384
2	26 (18)	−0.0574	0.0795	−0.2147
3	26 (18)	−0.1588	0.0779	−0.0306
4	26 (18)	−0.0416	0.0501	−0.0826
5	26 (18)	−0.0315	0.0660	−0.0531
6	26 (18)	−0.0549	0.0760	−0.1057
7	26 (−)	−0.0135	0.0085	0.0159
8	28 (18)	−0.0968	0.0750	−0.0794
9	30 (20)	0.0707	−0.0696	0.0482
10	32 (22)	−0.0705	0.0639	−0.1627
11	40 (28)	0.0427	−0.0379	0.0420
12	38 (26)	−0.0102	0.0401	−0.0374
13	26 (18)	−0.0181	0.0407	−0.0571
14	34 (24)	0.0239	−0.0466	0.0411
15	40 (28)	0.0553	−0.0955	0.0522
16[b]	40 (28)	−0.1132	0.0547	−0.0928
17	34 (24)	0.0610	−0.1410	0.0626
18[b]	34 (24)	−0.1018	0.0605	−0.1272

[a] Values in parentheses indicate the nominal number of π-electrons that reside on the main macrocyclic conjugation pathway (MMCP). [b] Möbius-twisted species.

Table 4 NICS values for porphycene and the molecular dianion

Species	NICS[a]/ppm
 Porphycene (**3**)	a: −14.31 b: −5.85 c: −15.24
 Porphycene molecular dianion ($\mathbf{3}^{2-}$)	a: −10.28 b: −10.32 c: +7.34

[a] NICS values taken from ref. 58. The computational level employed is GIAO-SCF/6-31+G*//B3LYP/6-31G*.

contribute much to the macrocyclic ring current, because the areas of all macrocyclic circuits are very large compared to those of local circuits. As a result, intense macrocyclic π-circulation is often observed along the macrocycle, the sense of which is determined by the sign of SSE or the nominal number of π-electrons that reside on the MMCP.

Let us survey briefly the magnetotropic situation in free-base porphine (**1**) and orangarin (**9**). The intensities of currents induced in individual circuits in **1** and **9** are given in Table 5, where positive and negative values indicate diamagnetic and paramagnetic currents, respectively. All circuits in **1** and all local circuits in **9** are diatropic, whereas all macrocyclic circuits in **9** are paratropic. Some macrocyclic circuits, such as **1e**, **1h** and **1j** in **1** and **9i**, **9m**, **9q** and **9t** in **9**, really sustain intense currents although CREs for them are fairly small in absolute value. These circuits sustain as intense π-currents as local five-site circuits. Of course, the MMCP sustains the intensest π-current among the macrocyclic circuits. In this sense, the MMCP is a representative of macrocyclic circuits. For ring-current distributions in **1** and **9**, see ref. 14, 16 and 18.

As has been seen, porphyrinoid π-systems are unique, in that macrocyclic and local aromaticity can be examined separately. Pyrrolic rings are the origin of local aromaticity, whereas π-bonds that link pyrrolic rings are under the sole influence of macrocyclic aromaticity. On a per π-bond basis, stabilization energy due to macrocyclic aromaticity is much smaller than that due to local aromaticity. Relatively small SSE is used to stabilize the entire macrocycle, whereas the large TRE-SSE difference can be used to stabilize local rings. Therefore, kinetic stability of a porphyrin molecule must be determined primarily by the degree of macrocyclic aromaticity. This is the main reason why macrocyclic aromaticity seems to be a determinant of kinetic stability for porphyrinoids. Note that the reactivity of a molecule is determined by the reactivity of the most reactive site in the molecule.[28–30] In unsubstituted porphyrinoid molecules, the least aromatic parts in the π-system are π-bonds that link local pyrrolic rings.

The 22π-electron delocalization model

On the basis of HOMA (harmonic oscillator model of aromaticity)[63] and NICS[61] values, Cyrański *et al.* argued that the global aromaticity of free-base porphine (**1**) is best represented as a 22π-electron delocalized subsystem.[64] This picture, reproduced in Fig. 6, was drawn by combining two pyrrole rings with the 18π-[16]annulene internal cross. In fact, they associated calculated HOMA and NICS values with individual rings but not with individual circuits. Jusélius and Sundholm then proposed the same 22π-electron pathway as the most important aromatic pathway in **1**.[40] They obtained this model by removing the C_2H_2 groups of the magnetically least aromatic 2H-pyrrole rings from the entire π-system. Therefore, it is not clear whether or not the 22π-electron delocalization model is compatible with the [18] annulene model.[65] Both were designed from somewhat different viewpoints.

With magnetic criteria of aromaticity, we cannot distinguish the effects of macrocyclic aromaticity distinctly from those of local aromaticity. NICS values and proton chemical shifts are affected not only by π-circulation induced along the macrocycle but also by local π-circulation induced at every pyrrole ring.[18] They also are affected by the way macrocyclic π-circulation bifurcates at every pyrrolic ring. In our view, the 22π-electron model emphasizes the importance of two types of highly diatropic circuits, **1a** and **1h**; **1a** is a local circuit of highest aromaticity and **1h** is a macrocyclic circuit of highest aromaticity. As can be seen from Table 5A, the intensest currents are induced in these two types of circuits.

Table 5 CREs for non-identical circuits in two free-base porphyrins and their divalent molecular ions

A. Free-base porphine (**1**).

		CRE/$\|\beta\|$		
Circuit	Multiplicity[a]	Dication	Neutral[b]	Dianion
1a	2	0.1462	0.0780 (0.2342)	0.1163
1b	2	0.0836	0.0571 (0.1720)	0.2455
1c	1	−0.0182	0.0050 (0.1179)	−0.0087
1d	2	−0.0017	0.0022 (0.0596)	−0.0068
1e	2	−0.0258	0.0082 (0.2174)	−0.0189
1f	1	0.0002	0.0009 (0.0254)	−0.0051
1g	4	−0.0023	0.0035 (0.1028)	−0.0145
1h	1	−0.0367	0.0131 (0.3890)	−0.0406
1i	2	0.0003	0.0013 (0.0409)	−0.0106
1j	2	−0.0032	0.0053 (0.1733)	−0.0303
1k	1	0.0004	0.0018 (0.0649)	−0.0218

B. Orangarin (**9**).

		CRE/$\|\beta\|$		
Circuit	Multiplicity[a]	Dication	Neutral[b]	Dianion
9a	1	−0.0182	0.1884 (0.5516)	0.1451
9b	2	−0.0404	0.1344 (0.3993)	0.1540
9c	2	0.0488	0.1516 (0.4467)	0.0952
9d	1	0.0032	−0.0023 (−0.0579)	0.0003
9e	1	0.0045	−0.0038 (−0.1079)	0.0008
9f	2	0.0005	−0.0011 (−0.0300)	0.0003
9g	2	0.0045	−0.0038 (−0.1080)	0.0008
9h	2	0.0007	−0.0017 (−0.0533)	0.0007
9i	2	0.0064	−0.0063 (−0.1969)	0.0019
9j	2	0.0007	−0.0017 (−0.0534)	0.0007
9k	2	0.0007	−0.0017 (−0.0534)	0.0007
9l	1	0.0000	−0.0004 (−0.0141)	0.0003
9m	1	0.0064	−0.0063 (−0.1970)	0.0019
9n	2	0.0010	−0.0027 (−0.0935)	0.0016
9o	2	0.0010	−0.0027 (−0.0935)	0.0016
9p	1	0.0000	−0.0007 (−0.0237)	0.0006
9q	1	0.0090	−0.0102 (−0.3520)	0.0043
9r	2	0.0010	−0.0027 (−0.0935)	0.0016
9s	2	0.0000	−0.0007 (−0.0237)	0.0006
9t	2	0.0014	−0.0043 (−0.1608)	0.0033
9u	2	0.0000	−0.0011 (−0.0402)	0.0012
9v	1	0.0000	−0.0011 (−0.0402)	0.0012
9w	1	0.0000	−0.0016 (−0.0663)	0.0024

[a] Number of identical circuits. [b] Each value in parentheses is the intensity of the current induced in the circuit, given in units of the benzene value; positive and negative values indicate diamagnetic and paramagnetic currents, respectively.

Hückel-like rule of macrocyclic aromaticity

We learned from the TRE *vs.* N_π plots in Fig. 3 how global aromaticity of each porphyrinoid species varies when it forms a molecular ion. We then proceed to examine the N_π dependence of SSE for individual porphyrinoids. Line plots of SSE against N_π for eight of the porphyrinoids are shown in Fig. 7, where arrows point to neutral species. These plots have two distinct regions in which the sign of SSE varies regularly; one is where N_π is very small ($N_\pi < 10$) and the other is where the molecular tetracation, dication, dianion and tetraanion, as well as the neutral species, are located. For all Hückel conformers (*i.e.*, all porphyrinoids but **16** and **18**), SSE is positive in sign for $N_\pi = 2$ and 6, but is negative for $N_\pi = 4$ and 8. For Möbius conformers **16** and **18**, the reverse holds true; SSE is negative for $N_\pi = 2$ and 6, but is positive for $N_\pi = 4$ and 8.

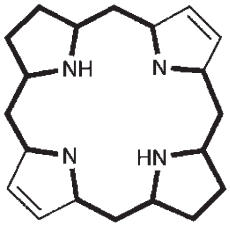


Fig. 6 The 22-π-electron model of free-base porphine (**1**).

SSEs for divalent molecular ions of **1**–**18** are listed in Table 3. We have seen that the sign of SSE for a neutral species is determined by the nominal number of π-electrons that reside on the MMPC. Table 3 tells us that, with the exception of *m*-benziporphyrin (**7**), SSEs for doubly charged molecular ions have a different sign from those of the neutral ones. That is, for most porphyrinoids with positive SSEs, the molecular dication and dianion have negative SSEs with paratropic macrocycles. For most species with negative SSEs, the reverse holds true. Such a regular change in the sign of SSE, together with the formal applicability of Hückel's [$4n$ + 2] rule to the MMCP of the neutral species, may be referred to as the Hückel-like rule of macrocyclic aromaticity.[66] When a porphyrinoid π-system is a neutral or doubly charged one, most macrocyclic circuits exhibit CREs of the same sign as that of the SSE. CREs for all circuits in the divalent molecular ions of free-base porphine (**1**) and orangarin (**9**) are added in Table 5. Some porphyrinoid molecular ions, such as those of **7**, however, violate the Hückel-like rule of macrocyclic aromaticity; **7** is a cross-conjugated porphyrin with no MMCP. SSEs are positive in sign both for **7** and $\mathbf{7}^{2-}$,

NICS values calculated for porphycene (**3**)[58] support the Hückel-like rule of macrocyclic aromaticity. As seen from Table 4, the NICS value at the center of the π-system is negative for the neutral molecule, but is positive for the molecular dianion ($\mathbf{3}^{2-}$). These values support our view that the neutral species sustains a diamagnetic current along the macrocycle, but that the dianion sustains a paramagnetic current along the macrocycle. Note that diamagnetic and paramagnetic π-circulation around the macrocycle correspond to positive and negative SSEs, respectively. NICS values at the centers of the pyrrolic rings are all negative both in **3** and $\mathbf{3}^{2-}$. These NICS values mean that all pyrrolic rings sustain diamagnetic currents both in the neutral species and in the molecular dianion. In line with these NICS values, **3** and $\mathbf{3}^{2-}$ is locally aromatic with large positive TRE-SSE differences. By the way, TRE for $\mathbf{3}^{2-}$ is 0.7564 $|\beta|$.

We previously pointed out that a certain group of large paracyclophane molecules obey the same Hückel-like rule of macrocyclic aromaticity.[66–68] These are macrocyclic π-systems consisting of four or more paraphenylene units linked circularly by an even number of ethylene fragments. Macrocycles of these molecules are weakly paratropic in the neutral state. Müllen *et al.* observed that the molecular dianions and tetraanions sustain diamagnetic and paramagnetic currents, respectively, along the macrocycles.[67] Shabtai *et al.* found that a diamagnetic

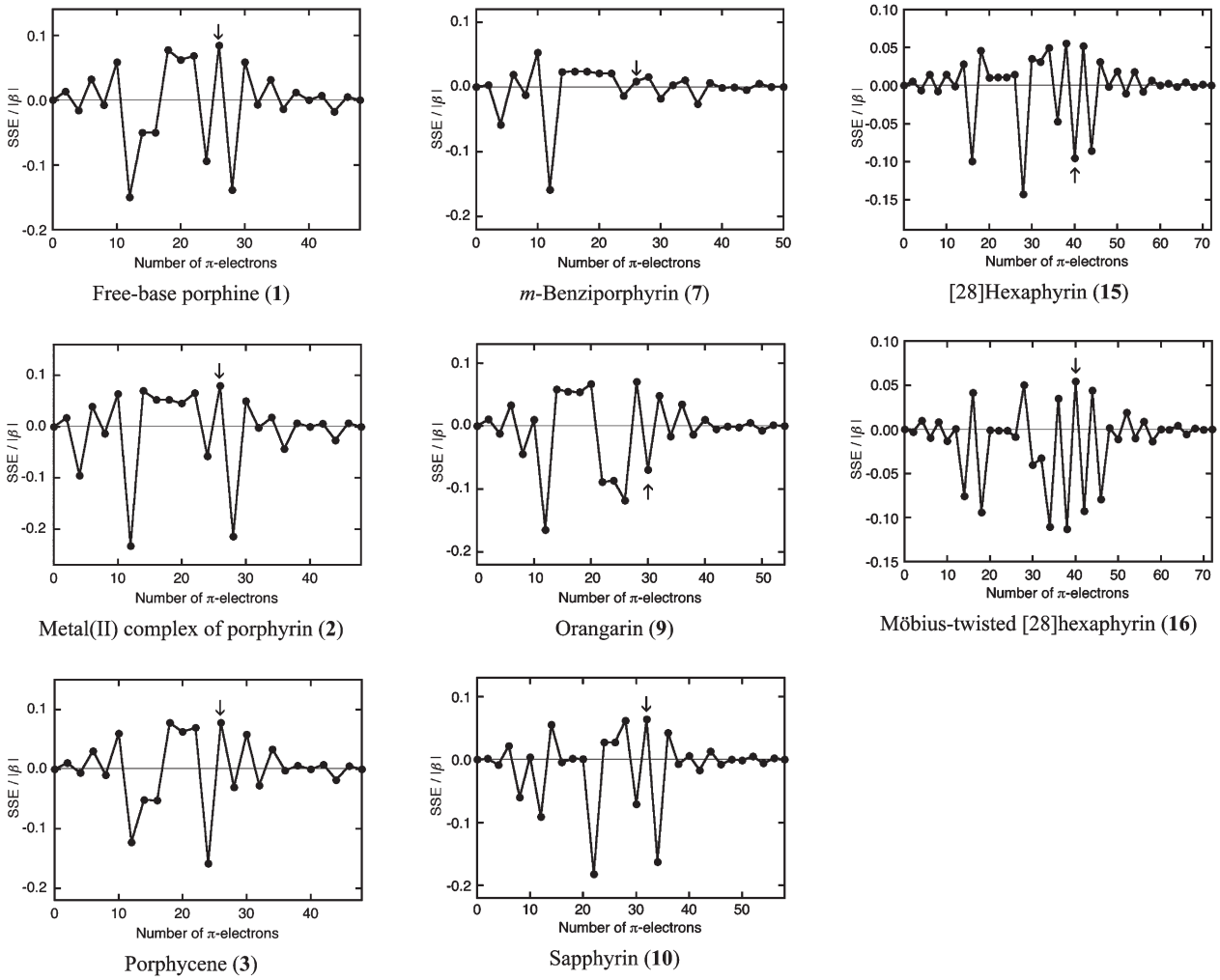


Fig. 7 SSEs for eight porphyrinoids, each as a function of the number of π-electrons (N_π). Arrows point to the neutral species.

current is again induced in the macrocycle when these molecular ions are further reduced to molecular hexaanions.[68]

4. Concluding remarks

Global and macrocyclic aromaticity of porphyrinoids were characterized by using our graph theory of aromaticity and ring-current diamagnetism. The sequential line plots of TRE against N_π for a variety of porphyrinoid species are very similar with four major extrema to those for five-membered heterocycles. This supports the view that five-membered rings are the main origin of global aromaticity. Macrocyclic circuits contribute significantly to macrocyclic π-circulation but modestly to global aromaticity. Macrocyclic aromaticity/antiaromaticity in oligopyrrolic macrocycles can be predicted by formally applying Hückel's [4n + 2] rule to an annulene-like MMCP. Such a bridged annulene model can be justified by examining the contribution of individual macrocyclic circuits to aromaticity. It should be noted that the bridged annulene model is a model for macrocyclic aromaticity and macrocyclic π-circulation, so it says nothing about global aromaticity. Based on the line plots of SSE against N_π for porphyrinoid species, a Hückel-like rule of macrocyclic aromaticity was found. Cross-conjugated porphyrinoids may be somewhat different in macrocyclic aromaticity from the typical free-base porphyrins.

Finally, one comment is made on our theory of aromaticity and ring-current diamagnetism[26–28,31,32,35,36] employed in this study. This theory is a totally analytic or exact one, in the sense that it was constructed without introducing any approximation nor any parametrization. However, it is not free from faults inherent in Hückel MO theory. This theory has so far been applied successfully to many polycyclic π-systems[26,27,31,32,35,36] including fullerenes[28] and a variety of porphyrinoids.[13–18] We evaluated various quantities without regarding substituents and bond-length alternation. This might have varied some numerical values.

Glossary of abbreviations

ASE	aromatic stabilization energy
BRE	bond resonance energy
CRE	circuit resonance energy
HMO	Hückel molecular orbital
HOMA	harmonic oscillator model of aromaticity

HOMO	highest occupied molecular orbital
MMCP	main macrocyclic conjugation pathway
MO	molecular orbital
NICS	nucleus-independent chemical shift
PAH	polycyclic aromatic hydrocarbon
SSE	superaromatic stabilization energy
TRE	topological resonance energy

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