Macrocyclic aromaticity in Hückel and Möbius conformers of porphyrinoids

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Macrocyclic aromaticity is one of the key concepts in porphyrin chemistry. The degree of macrocyclic aromaticity and the associated main macrocyclic conjugation pathway in Hückel- and Möbius-type porphyrinoids were determined using our recently proposed procedure based on bond resonance energy (BRE). All porphyrinoids with diatropic and paratropic macrocycles were found to have positive and negative superaromatic stabilization energies (SSEs), respectively. Main macrocyclic conjugation pathways predicted for various porphyrinoids were exactly the same as those predicted from the annulene model for porphyrinoids. Thus, macrocyclic aromaticity of Hückel and Möbius porphyrinoids has been rationalized successfully using an energetic criterion of aromaticity.

1. Introduction

Porphyrin chemistry is now in full bloom. A variety of porphyrinoid macrocycles have been prepared and characterized.[1–6] These porphyrinoids have often been viewed as bridged annulenes.[1–6] This naïve picture of porphyrinoids will be termed the annulene model. For example, Lash called free-base porphine Nature's [18]annulene, emphasizing that the macrocyclic 18π conjugation pathway must contribute predominantly to aromaticity.[4] Although the main origin of aromaticity in porphyrinoids later proved to be not macrocyclic conjugation but local pyrrolic rings,[6,7] it is still true that proton chemical shifts are primarily determined by macrocyclic conjugation.[1–7] Here and hereafter, part of aromaticity due to macrocyclic conjugation is referred to as superaromaticity or macrocyclic aromaticity.

Main macrocyclic circuits, such as an [18]annulene pathway in free-base porphine, are called main macrocyclic conjugation pathways. Those in free-base porphyrinoids never pass through amine nitrogens (>N-).[1–6] Such a main conjugation pathway has long been linked directly with macrocyclic aromaticity.[1–4] We recently proposed a general graph-theoretical approach to a main macrocyclic conjugation pathway in porphyrinoid π-systems.[6] The essence of this approach is to choose a π-bond with a larger bond resonance energy (BRE)[8–12] at every bifurcation in the macrocycle. Main macrocyclic conjugation pathways thus predicted formally supports the annulene model for porphyrinoids.[1–6]

Much attention has been paid to characterization of Möbius or singly half-twisted π-systems.[13–16] In 2003, Ajami *et al.* reported the first synthesis of a Möbius aromatic annulene, a [16]annulene derivative.[17] Since then, Möbius conformers of several porphyrinoids have been synthesized successfully.[18–24] In this study, we apply our BRE-based approach[6] to these Möbius and structurally related Hückel porphyrinoids to deepen our understanding of macrocyclic aromaticity and macrocyclic conjugation.[1–6,25] It is important to note that porphyrinoid aromaticity has not been examined from an energetic point of view.

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2. Theory

As properly stated by Dewar and others,[26–29] the term 'aromatic' describes molecules that benefit energetically from the delocalization of π electrons in closed circuits. We deal with global and macrocyclic aromaticity within the framework of Hückel molecular orbital theory.[6,7] As noted by Steiner and Fowler,[30] the distribution of the doubly-occupied π-orbitals in porphyrinoids can be well simulated by the 'coarse-grained' Hückel spectrum. Topological resonance energy (TRE) is used as an energetic criterion of global aromaticity.[28,29] A Möbius π-system can be designed readily by replacing the resonance integral for one of the π-bonds linking two adjacent rings by the negative of it.[13,14] The polyene reference for a Möbius conformer is exactly the same as that for the corresponding Hückel conformer.[14] Hückel parameters for heteroatoms proposed by Van-Catledge[31] are employed throughout this paper. We assume that the transition metal ions, such as rhodium(I) and palladium(II), are not included in the π-system and that nitrogen atoms coordinated to the metal ions are of imine (=N-) type.[6,7]

The definition of BRE is outlined for the benefit of the general reader.[8–12] A hypothetical π-system, in which a given π-bond (*e.g.*, a π-bond formed between the pth and qth atoms) interrupts cyclic conjugation, 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 a pair of resonance integrals between conjugated atoms p and q, and i is the square root of –1. In this π-system, no π circulation is expected to occur along the circuits that share the p–q π-bond in common. BRE for the p–q π-bond is given as a destabilization energy of this hypothetical π-system. In other words, BRE for a given π-bond represents the contribution of all circuits that share the bond to global aromaticity.[8–12] This quantity was originally defined to justify the isolated pentagon rule for fullerenes.[8]

Superaromatic stabilization energy (SSE) represents extra stabilization energy due to macrocyclic aromaticity.[6,7,32,33] For all porphyrinoids, SSE is equal to the BRE for any of the π-bonds that link adjacent pyrrolic or other rings.[6,7] Calculated BREs can be used for predicting or finding a main macrocyclic conjugation pathway in porphyrins.[6] When a given macrocyclic π-system has a positive SSE, the main macrocyclic conjugation pathway can

be traced by choosing a π-bond with a larger BRE at every bifurcation in the π-network. A main macrocyclic conjugation pathway primarily responsible for a negative SSE can be traced by choosing a π-bond with a smaller BRE at every bifurcation in the π-network. Note that not only TRE but also BRE and SSE belong to energetic criteria of aromaticity.

3. Results and discussion

Typical Möbius conformers of porphyrinoids so far synthesized and structurally related Hückel conformers[18–24] are graphically shown in Fig. 1–6. Here, **H** and **M** stand for Hückel and Möbius conformers, respectively. All Möbius conformers possess a twisted single-sided Möbius topology. We chose these six pairs of porphyrinoids for the present study. For simplicity, all substituents were ignored. We first survey experimental results so far reported on six Hückel–Möbius pairs of porphyrinoids briefly.[18–24] As will be seen below, porphyrin chemists used to predict macrocyclic aromaticity by means of proton NMR spectroscopy.

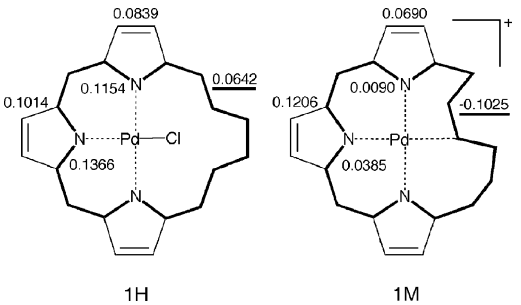

Fig. 1 BREs in units of $|\beta|$ for palladium(II) complexes of vacataporphyrin in Hückel (**1H**) and Möbius (**1M**) conformations. Main macrocyclic conjugation pathways are shown in bold.

In 2008, Pacholska-Dudziak *et al.* noticed that the coordination of palladium(II) to three pyrrolic rings of vacataporphyrin triggers a sequence of conformational changes.[22] They then obtained palladium(II) vacataporphyrin complexes in Hückel (**1H**) and Möbius (**1M**) conformations, which display ring-current diamagnetism (diatropicity) and paramagnetism (paratropicity), respectively.[22]

In the same year, Park *et al.* synthesized N-fused [24]pentaphyrin with a Hückel conformation (**2H**) and the rhodium(I) complex with a Möbius conformation (**2M**).[20] The Möbius conformation (**2M**) is fixed by rhodium(I) metalation. Although these molecules are heavily deviated from planarity, proton NMR spectra of **2H** and **2M** still features distinct paramagnetic and diamagnetic ring currents, respectively.[20]

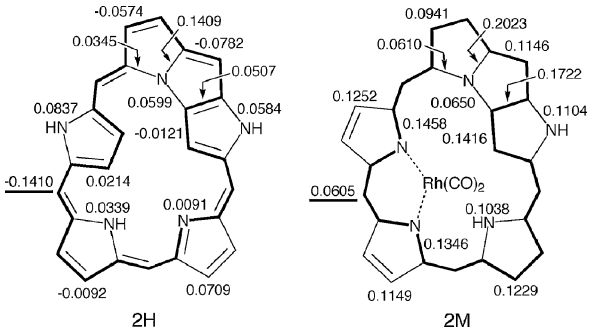

Fig. 2 BREs in units of $|\beta|$ for N-fused [24]pentaphyrin (**2H**) in Hückel conformation and the rhodium(I) complex (**2M**) in Möbius conformation. Main macrocyclic conjugation pathways are shown in bold.

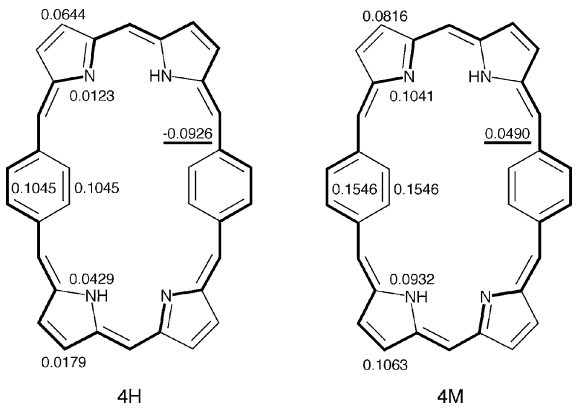

Fig. 4 BREs in units of $|\beta|$ for Hückel (**4H**) and Möbius (**4M**) conformers of di-*p*-benzi[28]hexaphyrin. Main macrocyclic conjugation pathways are shown in bold.

In 2008, Sankar *et al.* postulated that some *meso*-aryl-substituted [28]hexaphyrins in solution might exist largely as an equilibrium among several rapidly interconverting twisted Möbius diatropic conformers (**3M**), with a small amount of planar Hückel conformer (**3H**) with slightly higher energy and paratropic character.[24] In the solid state, they take either planar or Möbius-twisted conformers.[24]

In 2007, Stępień *et al.* reported the synthesis and properties of di-*p*-benzi[28]hexaphyrin.[18,21] This molecule exhibits a Möbius

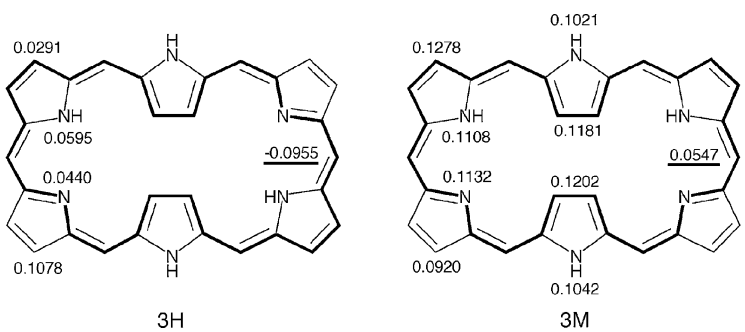

Fig. 3 BREs in units of $|\beta|$ for Hückel (**3H**) and Möbius (**3M**) conformers of [28]hexaphyrin. Main macrocyclic conjugation pathways are shown in bold.

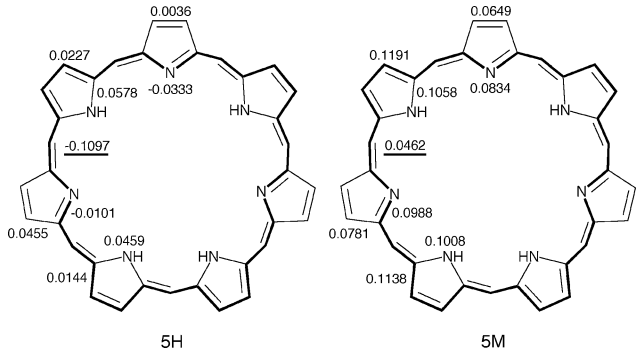

Fig. 5 BREs in units of $|\beta|$ for Hückel (**5H**) and Möbius (**5M**) conformers of [32]heptaphyrin. Main macrocyclic conjugation pathways are shown in bold.

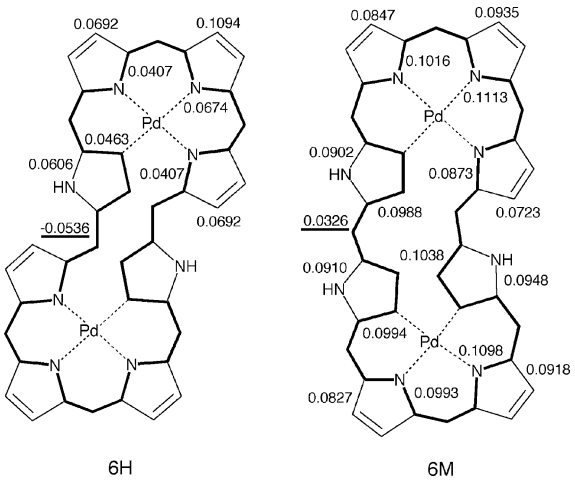

Fig. 6 BREs in units of $|\beta|$ for the bispalladium(II) complexes of [36]octaphyrin in Hückel (**6H**) and Möbius (**6M**) conformations. Main macrocyclic conjugation pathways are shown in bold.

conformation (**4M**) in the solid state but shows a dynamic Hückel–Möbius conformational interconversion in solution as evidenced by proton NMR spectroscopy.[18] Like many other large expanded porphyrins,[34] **4M** adopts a figure-eight configuration in the solid state. The Hückel conformer observable in solution is referred to as **4H**. Paratropicity of **4H** is evident from the proton chemical shifts.[18] However, **4M** displays proton chemical shifts characteristic of porphyrinoids devoid of macrocyclic aromaticity.[18]

In 2008, Saito *et al.* reported that the conformations of *meso*-aryl-substituted [32]heptaphyrins are dependent upon the substituents, solvent and temperature.[23] The pentafluorophenyl derivative take a figure-eight conformation in nonpolar solvents and in the crystalline state. This molecular structure is consistent with a twisted double-sided Hückel topology with C_2 symmetry. The Hückel conformer (**5H**) exhibit a diamagnetic ring current. On the other hand, the 2,6-dichlorophenyl derivative takes a twisted Möbius conformation (**5M**) both in solution and in the crystalline state. The proton NMR spectrum measured at low temperature was best interpreted in terms of the existence of several Möbius-type paratropic conformers.[23]

A bit earlier, Tanaka *et al.* found that Möbius macrocycles can be formed rather systematically by metalation of appropriate large *meso*-substituted expanded porphyrins.[19,21] Among Möbius macrocycles of this type is a bispalladium(II) complex of [36]octaphyrin (**6M**) with a twisted single-sided topology. They simultaneously obtained the Hückel conformer of the same complex (**6H**). Like **4M**, **6H** possesses a figure-eight structure with a twisted double-sided Hückel topology.[19] Conformers **6H** and **6M** exhibit distinct paramagnetic and diamagnetic ring current effects, respectively.[19]

Table 1 TREs and SSEs for Hückel and Möbius conformers of porphyrinoids. For molecular structures of these species, see Fig. 1–6

Species	TRE/$\|\beta\|$	SSE/$\|\beta\|$
1H	0.3468	0.0642
1M	0.1801	–0.1025
2H	0.4364	–0.1410
2M	0.6732	0.0605
3H	0.5371	–0.0955
3M	0.6743	0.0547
4H	0.5526	–0.0926
4M	0.6941	0.0490
5H	0.5520	–0.1097
5M	0.7079	0.0462
6H	0.7018	–0.0536
6M	0.7749	0.0326

Table 1 contains TREs and SSEs for the six pairs of porphyrinoids. BREs for all non-identical π-bonds are entered in Fig. 1–6. In these figures, BREs underlined represent SSEs. Positive and negative SSEs represent macrocyclic aromaticity and antiaromaticity, respectively. As stated earlier, TRE is a measure of global aromaticity. All species but **1M** are moderately aromatic with positive TREs. Even **1M** is still aromatic with a positive TRE although the aromaticity of the entire π-system is greatly suppressed by macrocyclic antiaromaticity. In general, macrocyclic antiaromaticity, if any, is not crucial for determining global aromaticity. This is why several porphyrinoids have been synthesized so far, irrespective of their macrocyclic aromaticity. Among the macrocycles studied, **1M**, **2M**, **3M**, **5M**, and **6M** are truly stable and isolable Möbius π-systems.

One should note that all diatropic porphyrinoids have positive SSEs, whereas all paratropic ones have negative SSEs. Thus, macrocyclic aromaticity/antiaromaticity, so far predicted from proton chemical shifts, has been rationalized on the basis of an energetic criterion of aromaticity. Diatropic porphyrinoids are thermodynamically stabilized by macrocyclic conjugation, whereas paratropic ones are thermodynamically destabilized by macrocyclic conjugation. This fact never means that porphyrinoids with negative SSEs have global antiaromaticity. Six porphyrinoids **1M**, **2H**, **3H**, **4H**, **5H** and **6H** are aromatic species with macrocyclic antiaromaticity.

Main macrocyclic conjugation pathways in all the twelve species, determined using our BRE-based procedure,[6] are shown in bold lines in Fig. 1–6. Main macrocyclic conjugation pathways in **1H** and **1M** are identical with Hückel and Möbius [17]annulene monoanions, respectively, both with 18 π-electrons. Those in **2H** and **2M** are identical with Hückel [24]annulene and the Möbius [23]annulene monoanion, respectively, both with 24 π-electrons. Main macrocyclic conjugation pathways in **3H** and **4H** are identical with Hückel [28]annulene, whereas those in **3M** and **4M** are identical with Möbius [28]annulene. Outer and inner π-bonds of two *para*-phenylene rings in **4H** and **4M** are topologically identical with the same BREs. Main macrocyclic conjugation

pathways in **5H** and **5M** are identical with Hückel and Möbius [32]annulenes with 32 π-electrons, respectively. Finally, those in **6H** and **6M** are identical with the Hückel [34]annulene dianion and the Möbius [35]annulene monoanion, respectively, each with 36 π-electrons. All these macrocyclic pathways are the same as those predicted by porphyrin chemists.[18–24]

For all porphyrinoids studied, the sign of SSE agree with that of TRE for the annulene that corresponds to the main macrocyclic conjugation pathway. Note that Hückel's $4n+2$ electron rule for aromaticity holds for Hückel annulenes and that the reverse of this rule holds for Möbius annulenes.[13,35,36] The present study revealed that these rules, applicable only to monocyclic π-systems, can formally be applied to main macrocyclic conjugation pathways in polycyclic porphyrinoids. In this context, Hosoya *et al.* found that the Hückel-like rule can likewise be applied to conjugated circuits in most polycyclic aromatic hydrocarbons.[37]

The magnitude of SSE depends roughly upon the size of the main macrocyclic conjugation pathway.[6] Larger main macrocyclic conjugation pathways have smaller positive or negative SSEs. This aspect of macrocyclic aromaticity reminds us of the fact that larger annulenes have smaller positive or negative TREs. Furthermore, it is well-known that the antiaromaticity of a given Hückel [4n]annulene is much greater than the aromaticity of Möbius [4n]annulene.[28,29] For example, the Hückel [32]annulene tetraanion is antiaromatic with a TRE of $-0.1445\ |\beta|$, whereas the Möbius [32]annulene tetraanion is aromatic with a TRE of $0.0482\ |\beta|$. Essentially the same trend is observable in the SSE associated with macrocyclic conjugation. In general, macrocyclic antiaromaticity in one conformer with a negative SSE is always greater than the macrocyclic aromaticity in another conformer with a positive SSE. Such an annulene analogy for porphyrinoids is sufficient to justify the reasonableness of the annulene model for porphyrinoids.

In porphyrin chemistry, a main macrocyclic circulation pathway is conceptually similar to a main macrocyclic conjugation pathway. As has been seen above, a main macrocyclic conjugation pathway can be predicted on the basis of the annulene model. A main macrocyclic conjugation pathway always avoids all amine nitrogens but pass through all imine nitrogens.[6] However, it is not always identical with a main macrocyclic conjugation pathway. For example, main macrocyclic conjugation pathways in two paratropic expanded porphyrins, orangarin[38] and amethyrin,[30] are not identical with their respective main macrocyclic circulation pathways,[6] the latter of which lie along the inner periphery, passing through all nitrogen atoms, including amine nitrogens.[30,38] In these porphyrinoids, a paramagnetic current induced along the macrocycle is disturbed by the local diamagnetic currents induced in the pyrrolic rings; local diamagnetic currents apparently intensify the paramagnetic current that flow along the periphery of the inner cavity. Our BRE-based approach is free from such a disturbance and so is a useful interpretative tool for macrocyclic aromaticity.

We have pointed out repeatedly that, if the minimum BRE (min BRE) in a π-system is smaller than $-0.100\ |\beta|$, the molecule will probably be kinetically unstable or chemically reactive.[8–10] In this sense, **1M**, **2H** and **5H** must be kinetically unstable with large negative SSEs. Nevertheless, they were prepared successfully.[20,22] In fact, these macrocycles are heavily distorted to suppress macrocyclic conjugation.[18–22] This must be why these three species are kinetically stable. Considering that macrocyclic antiaromaticity is sometimes suppressed in porphyrinoid π-systems,[6] **4M** is a rare species in which not macrocyclic antiaromaticity but macrocyclic aromaticity is effectively suppressed by torsional strain. Torsional strain in this species presumably resulted in insufficient overlap of $2p_z$ orbitals and then in the loss of macrocyclic aromaticity;[18] stabilization of the Möbius conformation must be accompanied by torsional strain.

Finally, one comment should be made on the figure-eight configuration of large porphyrinoid macrocycles. We previously showed that the intensity of the current induced in a given circuit is proportional to the aromatic stabilization energy arising from the circuit, multiplied by the area of the circuit.[39] If a given macrocycle adopts a figure-eight configuration, the signed areas enclosed by macrocyclic circuits must be much smaller than those in round or oval configurations. Such conformers must sustain more or less weaker macrocyclic ring currents.[39]

4. Concluding remarks

A main macrocyclic conjugation pathway and SSE obtained within the same theoretical framework constitute the essence of macrocyclic aromaticity in Hückel- and Möbius-type porphyrinoids. Rationalization of macrocyclic aromaticity has now been attained on the basis of energetic criteria of aromaticity. A main macrocyclic conjugation pathway is nothing other than a representative of macrocyclic circuits. In fact, there are many macrocyclic circuits in porphyrinoid π-systems, all of which contribute more or less to macrocyclic aromaticity. For example, **6H** and **6M** has as many as $256\ (=2^8)$ macrocyclic circuits. Hückel's $4n + 2$ π-electron rule of aromaticity can formally be applied to main macrocyclic conjugation pathways. In this context, the conventional annulene model proved to provide a reasonable but qualitative interpretation of macrocyclic aromaticity in porphyrinoids. Rzepa pointed out that large expanded porphyrins may adopt different solution and solid-state conformations, among which some must have half-twisted Möbius macrocycles.[25]

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References

1 E. Vogel, *Pure Appl. Chem*, 1993, **65**, 143.
2 B. Franck and A. Nonn, *Angew Chem. Int. Ed. Engl.*, 1995, **34**, 1795.
3 A. Jasat and D. Dolphin, *Chem. Rev*, 1997, **97**, 2267.
4 T. D. Lash, *Synlett*, 2000, 279.
5 J. L. Sessler and D. Seidel, *Angew. Chem. Int. Ed*, 2003, **42**, 5134.
6 J. Aihara, *J. Phys. Chem. A*, 2008, **112**, 5305.
7 J. Aihara, E. Kimura and T. M. Krygowski, *Bull. Chem. Soc. Jpn*, 2008, **81**, 826.
8 J. Aihara, *J. Am. Chem. Soc*, 1995, **117**, 4130.
9 J. Aihara, *J. Phys. Chem*, 1995, **99**, 12739.
10 J. Aihara, *J. Chem. Soc. Perkin Trans. 2*, 1996, 2185.
11 J. Aihara, T. Ishida and H. Kanno, *Bull. Chem. Soc. Jpn*, 2007, **80**, 1518.
12 M. Makino and J. Aihara, *Phys. Chem. Chem. Phys.*, 2008, **10**, 591, Electronic Supplementary Information.
13 E. Heilbronner, *Tetrahedron*, 1964, 1923.
14 J. Aihara, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1788.

15 C. Castro, C. M. Isoborn, W. L. Karney, M. Mauksch and P. v. R. Schleyer, *Org. Lett.*, 2002, **4**, 3431.
16 H. S. Rzepa, *Chem. Rev*, 2005, **105**, 3697.
17 D. Ajami, O. Oeckler, A. Simon and R. Herges, *Nature*, 2003, **426**, 819.
18 M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz and L. Szterenberg, *Angew. Chem. Int. Ed*, 2007, **46**, 7869.
19 Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim and A. Osuka, *Angew. Chem. Int. Ed*, 2008, **47**, 681.
20 J. K. Park, Z. S. Yoon, M.-C. Yoon, K. S. Kim, S. Mori, J.-Y. Shin, A. Osuka and D. Kim, *J. Am. Chem. Soc*, 2008, **130**, 1824.
21 N. Jux, *Angew. Chem. Int. Ed*, 2008, **47**, 2543.
22 E. Pacholska-Dudziak, J. Skonieczny, M. Pawlicki, L. Szterenberg, Z. Ciunik and L. Latos-Grażyński, *J. Am. Chem. Soc*, 2008, **130**, 6189.
23 S. Saito, J.-Y. Shin, J. M. Lim, K. S. Kim, D. Kim and A. Osuka, *Angew. Chem. Int. Ed*, 2008, **47**, 9657.
24 J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim and A. Osuka, *J. Am. Chem. Soc*, 2008, **130**, 13568.
25 H. S. Rzepa, *Org. Lett*, 2008, **10**, 949.
26 M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc*, 1969, **91**, 789.
27 B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc*, 1971, **93**, 305.
28 J. Aihara, *J. Am. Chem. Soc*, 1976, **98**, 2750.
29 I. Gutman, M. Milun and N. Trinajstić, *J. Am. Chem. Soc*, 1977, **99**, 1692.
30 E. Steiner and P. W. Fowler, *Org. Biomol. Chem*, 2006, **4**, 2473.
31 F. A. Van-Catledge, *J. Org. Chem*, 1980, **45**, 4801.
32 J. Aihara, *J. Am. Chem. Soc.*, 1992, **114**, 865.
33 J. Aihara, *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 237.
34 T. D. Lash, *Angew. Chem. Int. Ed.*, 2000, **39**, 1763.
35 E. Hückel, *Z. Phys.*, 1931, **70**, 204.
36 V. I. Minkin, M. N. Glukhovtsev, and B. Ya. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley-Interscience, New York, 1994, Ch. 3.
37 H. Hosoya, H. Hosoi and I. Gutman, *Theor. Chim. Acta*, 1972, **38**, 37.
38 E. Steiner and P. W. Fowler, *Org. Biomol. Chem*, 2004, **2**, 34.
39 J. Aihara, *J. Am. Chem. Soc.*, 2006, **128**, 2873.