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Deciphering Aromaticity in Porphyrinoids via Adaptive Natural Density Partitioning†

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The adaptive natural density partitioning (AdNDP) method has been applied for the first time to porphyrinoids in order to describe their aromaticity. The analysis of π -electron system reveals that aromaticity of annulene originates from $6\text{-}\pi$ -electron delocalization, while aromaticity of porphyrin can be better described in terms of local aromaticities of the appended $6\text{-}\pi$ -electron pyrrolic heterocycles and $6\text{-}\pi$ -electron central fragment. The patterns of chemical bonding for porphyrinoids obtained by AdNDP are consistent with chemical intuition and lead to unique and compact graphic formulas.

Introduction

Porphyrins are macrocyclic compounds that have attracted much attention because of their unique structures and a wide spectrum of very useful physicochemical and biological properties, such as anion binding, stabilization of metal ions with unusual oxidation states, electron transfer, and construction of peculiar supramolecular assemblies. However, despite the successful syntheses of various porphyrinoids and their analogues, there is still the contentious debate between chemists about the generally accepted description of aromaticity in such complicated macrocyclic systems. The Hückel rule¹ for aromaticity, stating that the presence of $[4n + 2]$ conjugated π electrons result in the formation of a stable aromatic compound, has played an important role in the development of diverse porphyrinoid chemistry since the early 1930s. Hence, the correct description of aromaticity and chemical bonding is vital for predicting new members of the porphyrin family and explaining their properties. In 1962 Sondheimer et al.² identified for the first time the resemblance between porphyrin and [18]annulene, proposing the interpretation of porphine structure as a multiple-bridged aromatic diaza[18]annulene system: „porphine and the derived porphyrins, as well as the phthalocyanines, are in fact the first known 18-electron systems related to [18]annulene.” Later, Vogel et al.,³ using annulene-like description of porphyrins, demonstrated the application of the Hückel $[4n + 2]$ π aromaticity rule for various porphyrin homologues that has been quite helpful for the synthetic preparation of different porphyrinoids.⁴ Lash et al.^{5a} has recently synthesized dideazaporphyrin – the simplified component of a porphyrin, which lacks two of the pyrrole rings. It has also been proposed that this compound should act as a modified [18]annulene, and the prominent diatropic shifts in the ¹H NMR spectrum as well as the X-ray structure, which exhibits a nearly planar system,

support that notion. The authors therefore concluded: “the aromatic characteristics of porphyrins clearly result from a number of features, but the essence of these properties appears to be encapsulated in the diaza[18]annulene substructure”.^{5a} However, despite the viability of the [18]annulene representation for porphyrinoid aromaticity, it has been increasingly questioned by theoretical chemists.

To date, there are a lot of computational models developed for the description of aromaticity in porphyrins, which are usually based on energetic, geometric, and magnetic criteria.⁶⁻¹⁵ In 1998, Schleyer et al.,⁶ using analysis of experimental bond lengths and computed nuclear independent chemical shifts (NICS) values, proposed that a more appropriate description of the porphyrin moiety should be a 22 π -electron macrocycle with two C_2H_2 exocyclic bridges. According to this model, the NH groups are an integral part of the aromatic system and not just the inert bridging groups as suggested by the classic [18]annulene representation. However, Fowler et al.,⁷ using ipsocentric current-density mapping techniques, suggested that the classic [18]annulene model of free base porphyrin is the most appropriate one. Aihara's studies based on the graph theory of aromaticity, have indicated that the aromatic characteristics of porphyrins are mainly due to the individual pyrrolic subunits.⁸ The most recently published Schleyer's work⁹ also shows that porphyrinoid aromaticity is not due primarily to the macrocyclic π conjugation of the corresponding annulene perimeters, and the appended 6π electron heterocycles of porphyrinoids confer aromaticity much more effectively than the macrocyclic $[4n + 2]$ π electron conjugations.

As one may see, there is a disagreement between synthetic chemists and theoreticians, probably because there is no simple, intuitive, and at the same time physically precise explanation of aromaticity in porphyrinoids. In the recent highlight, Bröring, summarizing different views on the aromaticity in porphyrinoids, calls theoreticians for providing more

clarification on the origin of aromaticity in porphyrins.¹⁶ We now respond. In the current study we propose our model of π electron system and aromaticity in annulenes and porphyrinoids, using adaptive natural density partitioning (AdNDP) approach.¹⁷ This approach leads to partitioning of the charge density of a molecule into elements with the highest-possible degree of localization of electron pairs such as the n -center two-electron (nc -2e) bonds, which include core electrons, lone pairs (LPs), 2c-2e bonds, etc. If some portion of the density cannot be localized in this manner, it is represented using completely delocalized objects, which are associated with the concepts of aromaticity and antiaromaticity. From this point of view, AdNDP achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. Additionally, our AdNDP approach has demonstrated effectiveness in the description of aromaticity in rather complicated chemical systems, such as graphene,¹⁸ coronene,¹⁹ isocoronene, circumcoronene,²⁰ and other organic molecules¹⁹ as well as silabenzenes,²¹ boron clusters²², and triple-decker sandwich complexes.²³

Results and discussion

In the present study, we use the AdNDP approach for the analysis of the molecular orbital wave function of the selected porphyrinoid macrocycles, including [18]annulene, dideazaporphyrin, [18]porphyrin, and dihydrodideazaporphyrin. According to our AdNDP analysis all σ bonds are well represented by classical two center – two electron (2c-2e) bonds and will not be discussed here.

Annulene $C_{18}H_{18}$ is an aromatic hydrocarbon with 18 π -electrons. According to the Hückel $[4n + 2]$ rule, its 18 π -electron system should be delocalized, resulting in a fully conjugated and planar structure with D_{6h} symmetry. Indeed, the X-ray diffraction analysis of $C_{18}H_{18}$ made by Hirshfeld et al.²⁴ yielded a roughly planar centrosymmetric molecule. The corresponding structures have also been proposed for [18]annulene²⁵ with the emphasis on the presence of 18 π -electron delocalized bonding in this molecule (Fig. 1, structures I and II). However, in spite of the fact that [18]annulene shows prominent aromatic features (large resonance energies and significant nuclear magnetic resonance ring currents), its reactivity more closely resembles a conjugated polyene rather than an aromatic hydrocarbon.² The application of AdNDP for $C_{18}H_{18}$ leads to the π bonding pattern shown in Fig. 1. Surprisingly, AdNDP recovered six three center – two electron (3c-2e) π bonds with an occupation number (ON) of 1.92 |e| at the periphery of [18]annulene, and three 18c-2e π bonds with ON = 2.00 |e| delocalized over all the carbon atoms. Thus, according to our analysis we believe that only 6 π electrons (satisfying the $[4n + 2]$ rule for aromaticity with $n = 1$) are responsible for the aromatic character of $C_{18}H_{18}$, whereas the remaining 12 π electrons form six conjugated 3c-2e π bonds, which might be in charge of the observed polyene-like chemical properties of [18]annulene.² The appropriate symbolic representation (Fig. 1, III) with conjugated 3c-2e π bonds is consistent with the appreciable C-C bond length alternation from 1.382 Å for 12 inner C-C bonds to 1.419 Å for 6 outer C-C bonds confirmed experimentally for this molecule.²⁴ However, Schleyer et al.,²⁶ using the ¹H NMR chemical shifts

and energy computations with BHLYP²⁷ and KMLYP²⁸ methods, suggested that [18]annulene prefers C-C bond-length alternation and C_2 symmetry, rather than D_{6h} symmetry. The application of AdNDP to the less symmetric (C_2) bond-alternate [18]annulene yielded π -bonding picture (see Fig. S1, ESI†) analogous to that of D_{6h} symmetric [18]annulene, which further proves the robustness of AdNDP method.

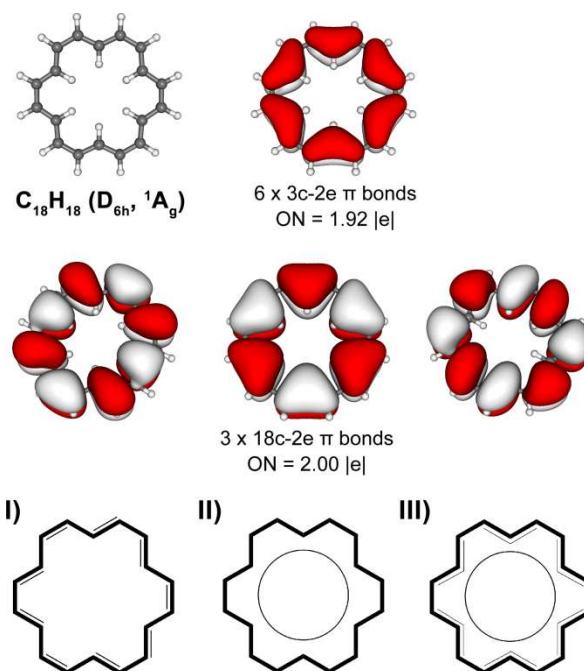


Fig. 1. AdNDP π bonding pattern for [18]annulene. The corresponding point group symmetry and spectroscopic state are given in parenthesis. I), II) possible bond structures proposed for [18]annulene; III) symbolic representation of [18]annulene according to AdNDP. Here and elsewhere three center – two electron (3c-2e) bonds and delocalized bonding in the AdNDP symbolic representation are depicted with bend lines and circles, respectively.

Dideazaporphyrin $C_{20}H_{16}N_2$ can be considered as structurally midway between [18]annulene and porphyrin. As it was discussed above, this molecule should behave similar to [18]annulene.⁵ Thus, our analysis revealed the bonding picture, which is almost identical to that of [18]annulene (Fig. 2), apart from the C=C bonds (ON = 1.86 |e|) of the corresponding heterocyclic rings. According to the AdNDP, the 18 π electron bonding framework of dideazaporphyrin consists of six peripheral 3c-2e π bonds (ON = 1.90-1.95 |e|), where two of them involve nitrogen atoms of the heterocyclic rings; and three completely delocalized 18c-2e π bonds with ON = 2.00 |e|. Hence, we may conclude that aromaticity of $C_{20}H_{16}N_2$ arises from 6 π electron core conjugations similar to what we observe for [18]annulene (Fig. 1). Interestingly, Schleyer's results, based on the block-localized wave function (BLW) calculations, show similar aromatic stabilization energies per carbon (ASE's) for dideazaporphyrin (+32.1 kcal/mol) and [18]annulene (+25.0 kcal/mol).⁹ The corresponding symbolic representations of $C_{20}H_{16}N_2$ in the form of resonance and AdNDP structures are depicted in Fig. 2: structures I and II, respectively.

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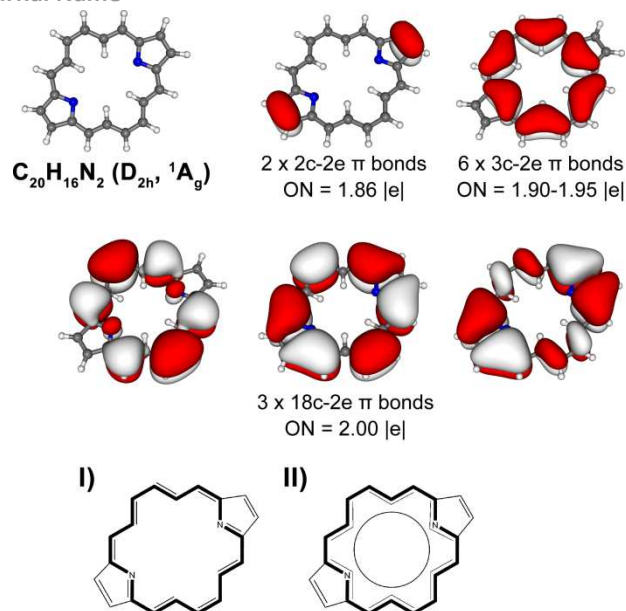


Fig. 2. AdNDP π bonding pattern for dideazaporphyrin. The corresponding point group symmetry and spectroscopic state are given in parenthesis. I) possible resonance structure proposed for dideazaporphyrin; II) symbolic representation of dideazaporphyrin according to AdNDP.

As the parent compound of the porphyrin series, [18]porphyrin $C_{20}H_{14}N_4$ occupies a unique position among other porphyrinoids. An X-ray crystallographic structure determination has been reported for the free base of porphine by Webb et al.²⁹ and the structure can be summarized briefly as the macrocyclic ring (Fig. 3) of four pyrroles alternately linked with four methine groups. Representative porphyrin structures illustrating two frequently used models for porphyrinoid aromaticity are shown in Fig. 3 (structures I and II). Structure I (Fig. 3, I), proposed by Vogel,³ describes aromaticity in terms of the [18]annulene model with the involvement of the 18 π electrons in the main conjugation pathway, thus obeying the $[4n + 2]$ rule with $n = 4$. In contrast, Schleyer's model⁶ II (Fig. 3, II) indicates that all four pyrrole rings are incorporated into the aromatic system with the 22 π electrons, including the nitrogen electron lone pairs of the pyrrole subunits. The results of our AdNDP analysis and the corresponding symbolic representation of [18]porphyrin (structure III) are shown in Fig. 3. As expected, AdNDP revealed two localized C=C bonds (ON = 1.81 |e|) of the dehydropyrrolic rings of $C_{20}H_{14}N_4$. Therefore, these bonds do not participate in aromaticity and can be viewed as exocyclic "ethylenic bridges" similar to those of dideazaporphyrin (Fig. 2). However, instead of six 3c-2e peripheral π bonds present in [18]annulene and dideazaporphyrin, the AdNDP analysis established only two 3c-2e π bonds (ON = 1.96 |e|), which are reminiscent of the two C-N-C 3c-2e bonds in dideazaporphyrin. The delocalized π bonding pattern responsible for aromaticity in porphyrin was found to be quite interesting. According to our results, it comprises three aromatic systems, two of which represent pyrroles with three delocalized 5c-2e π bonds with ON = 2.00 |e| (satisfying the $[4n + 2]$ rule for aromaticity with $n = 1$) and the third one is the larger heterocycle involving three 16c-2e π bonds with ON = 1.90 |e| (satisfying the $[4n + 2]$ rule for aromaticity with $n = 1$) delocalized over the central fragment of a porphyrin molecule (Fig. 3). Hence, we can make a conclusion that aromaticity in porphyrin can be better described

in terms of local aromaticities of two pyrrole rings and the central larger heterocyclic fragment. The picture of π chemical bonding (Fig. 3) shows that aromaticity in porphyrin has similar features with [18]annulene, i.e., the central porphyrin fragment involves three delocalized bonds as in [18]annulene, however, porphyrin aromaticity is different from [18]annulene aromaticity with respect to the presence of two appended 6 π electron pyrrolic subunits. Indeed, the total NICS(0) _{π zz} values, computed at the heavy atom center, for porphyrin (-47.3 ppm), dideazaporphyrin (-43.5 ppm), and [18]annulene (-47.9 ppm) are approximately the same, while the calculated aromatic stabilization energy of porphyrin (+70.9 kcal/mol) has the highest value.⁹ Thus, the description of aromaticity in porphyrin (model III) based on the results of the AdNDP analysis expresses the multifaceted nature of aromaticity similar to model II, however, at the same time local aromaticity of the central 16 atom fragment of porphyrin closely resembles the 6- π -electron pathway found in [18]annulene (Fig. 1).

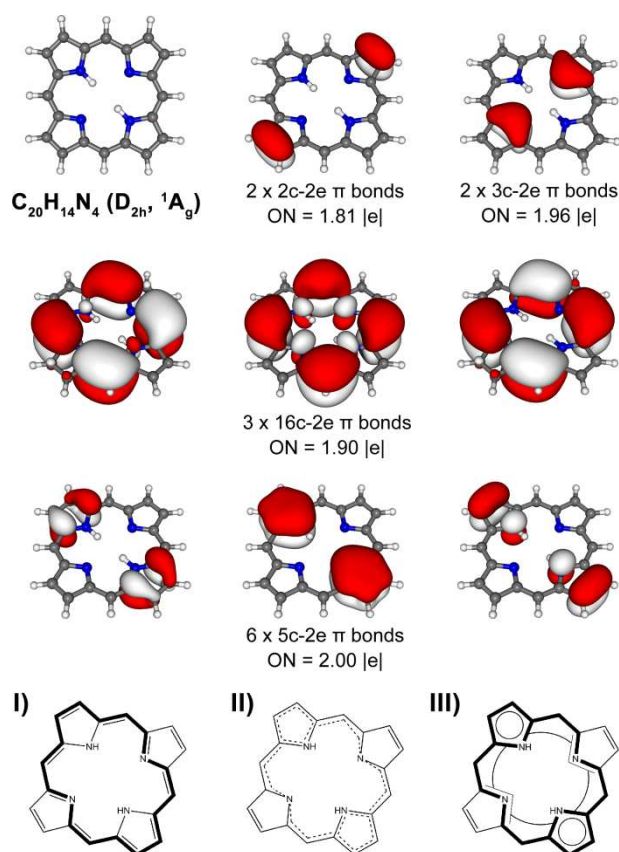


Fig. 3. AdNDP π bonding pattern for porphyrin. The corresponding point group symmetry and spectroscopic state are given in parenthesis. I), II), III) representative porphyrin structures illustrating three different models for porphyrinoid aromaticity, where I) shows the 18- π -electron delocalization, II) - the 22- π -electron delocalization, and III) - the three local 6- π -electron delocalizations recovered by AdNDP.

So far, our AdNDP approach worked well for the description of aromaticity and chemical bonding in aromatic $[4n + 2]$ porphyrinoids. However, there are plenty of examples of stable and experimentally obtained antiaromatic macrocyclic $[4n]$ annulenic π conjugated porphyrins, which show the opposite upfield/downfield 1H NMR chemical shifts for the outer/inner protons.³⁰ Hence, in order to further confirm the

validity of our approach, we performed AdNDP analysis for the representative antiaromatic porphyrinoid system – dihydrodiazaporphyrin⁵ $C_{20}H_{18}N_2$, which adopts quasi-planar structure (Fig. 4). According to the AdNDP results, there are six polyene-like 2c-2e C-C π bonds (ON = 1.82-1.85 |e|, superimposed on the central molecular framework) and three delocalized 5c-2e π bonds with ON = 2.00 |e| on each pyrrolic subunits. The deviations of the occupation numbers of the 2c-2e C-C π bonds from the ideal value of 2.00 |e| are signatures of the conjugation between the recovered π bonds. This bonding picture shows that despite having 24 π electrons (satisfying the 4n rule for antiaromaticity), dihydrodiazaporphyrin (Fig. 4) is locally aromatic molecule with respect to two aromatic pyrrolic fragments. The central core of dihydrodiazaporphyrin does not contain any delocalized π bonds and can be better described in terms of peripheral localized 2c-2e π bonds. Thus, we believe that the presence of aromatic pyrrole rings and obscure antiaromaticity of the central molecular fragment (six π bonds in $C_{20}H_{18}N_2$ were found to have more localized, rather than delocalized character) can explain the peculiar viability of some successfully synthesized Hückel antiaromatic porphyrinoids which are stable in spite of the fact that they have net 4n π electron counts.³⁰

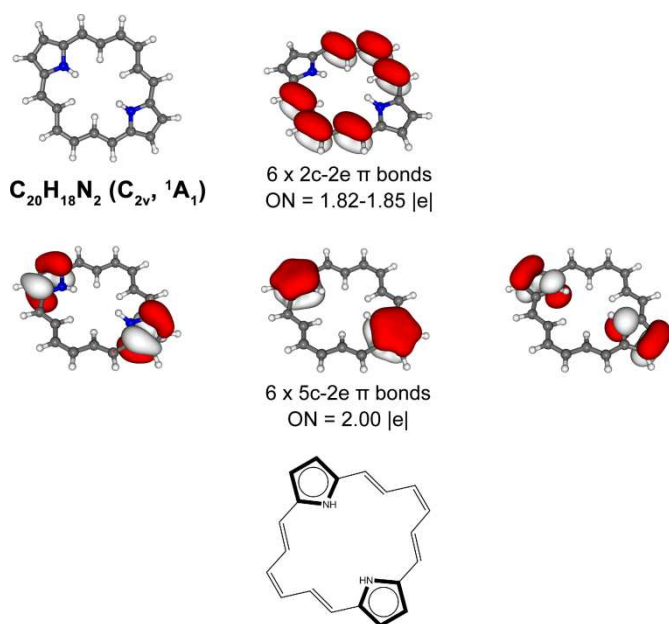


Fig. 4. AdNDP π bonding pattern and symbolic representation of antiaromatic dihydrodiazaporphyrin. The corresponding point group symmetry and spectroscopic state are given in parenthesis.

Experimental section

The detailed description of the AdNDP algorithm developed by Zubarev and Boldyrev can be found elsewhere.¹⁷ From the computational point of view, AdNDP is a generalization of the NBO analysis by Weinhold.³¹ AdNDP performs analysis of the first-order reduced density matrix with the purpose of obtaining its local block eigenfunctions with optimal convergence properties for describing the electron density. The local blocks of the first-order reduced density matrix correspond to the sets of n atoms (from one to all the atoms of the molecule) that are tested for the presence of a two-electron object (nc-2e bonds, including core electrons and lone pairs as a special case of $n = 1$) associated with this particular set of n atoms. The n atomic

sets are formed and checked in an exhaustive manner, so that the recovered nc-2e bonding elements always correspond to the point group symmetry of the system after these bonding elements are superimposed onto the molecular frame. For the given n atomic block those eigenvectors are accepted whose occupation numbers (eigenvalues) exceed the established threshold value, usually close to 2.00 |e|. Thus, Lewis's idea of an electronic pair as the essential element of bonding is preserved. The AdNDP procedure is numerically efficient because it involves only a series of diagonalizations of density matrix blocks. It is unbiased in the sense that no preliminary ideas of the bonding pattern are required to perform analysis. The AdNDP code is a stand-alone program that uses output from Gaussian 09. The geometry optimization and normal-mode analysis for the studied systems were carried out using the hybrid density functional B3LYP³² method with the 6-311++G** basis set³³ as implemented in the Gaussian 09 software package.³⁴ The density matrix used for the basis of the natural atomic orbitals as well as for the transformation between atomic orbital and natural atomic orbital basis sets, which are used by the AdNDP program, was generated at the B3LYP/3-21G level of theory by means of the NBO code³⁵ incorporated into Gaussian 09. It is known that the results of NBO analysis do not generally depend on the quality of the basis set, so the choice of the level of theory for the AdNDP application is adequate. The visualization of the results of the calculations was performed by using MOLEKEL 5.4.0.8.³⁶

Conclusions

In summary, we presented a new approach for the description of aromaticity in porphyrinoids. It was found that [18]annulene has only three completely delocalized π bonds associated with its aromaticity. Other 12 π electrons are in fact responsible for the conjugated 3c-2e π bonds formation, which can be likely manifested by polyene-like properties of [18]annulene. The results of our AdNDP analysis for porphyrin demonstrate that the appended 6 π aromatic sextets together with the 6 π aromatic core molecular fragment of porphyrin confer aromaticity much more efficiently than the “bridged [18]annulene” model. The AdNDP representations of porphyrinoids are novel and consistent with geometrical parameters of the studied molecules. It is also worthy to note that the patterns of chemical bonding recovered by AdNDP comply with chemical intuition and lead to unique compact graphic formulas. The significant advancement made in the current study is that the bonding patterns and formulas are derived from the MO wave function via a unified and well-defined quantum chemical procedure. Although the proposed assessment of aromaticity in porphyrinoids is practically based on qualitative analysis, the obtained π bonding pictures are generally in agreement with the results of quantitative theoretical approaches, such as NICS,^{6,9} BLW⁹ and current-density maps⁷ techniques. Since the presented approach combines both simplicity and quantum-chemical background, we believe that our representation of aromaticity in porphyrinoids would be clear for both preparative organic chemists and theoreticians. Hence, the results of our work can provide a new look at the diverse chemistry of porphyrinoids and might be helpful in understanding and rational design of novel porphyrinoid compounds.

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Notes and references

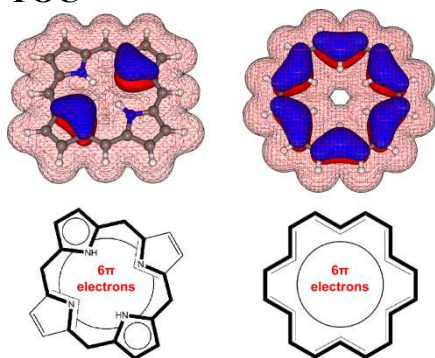
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†Electronic supplementary information (ESI) available: AdNDP analysis for C₂ symmetric [18]annulene. Cartesian coordinates of all studied structures at the B3LYP/6-311++G** level of theory. See DOI:

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