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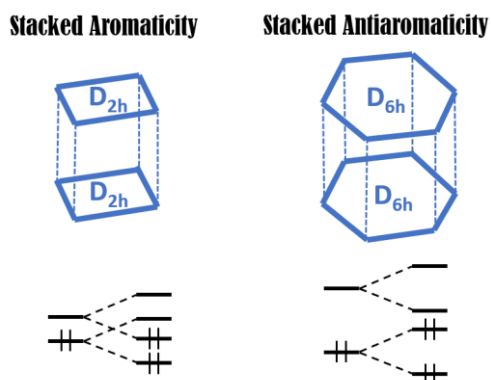
Hückel Molecular Orbital Analysis for Stability and Instability of Stacked Aromatic and Stacked Antiaromatic Systems

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TOC Graphic



Abstract

Face-to-face stacking of aromatic compounds leads to stacked antiaromaticity, while that of antiaromatic compounds leads to stacked aromaticity. This is a prediction with a long history: in the late 2000s, the prediction was confirmed by high-precision quantum chemical calculations, and finally, in 2016, a π -conjugated system with stacked aromaticity was synthesized. Several variations have since been reported, but essentially they are all the same molecule. To realize stacked aromaticity in a completely new and different molecular system and to trigger an extension of the concept of stacked aromaticity, it is important to understand the origin of stacked aromaticity. The Hückel method, which has been successful in giving qualitatively correct results for π -conjugated systems despite its bold assumptions, is well suited for the analysis of stacked aromaticity. We use this method to model the face-to-face stacking systems of benzene and cyclobutadiene molecules and discuss their stacked antiaromaticity and stacked aromaticity on the basis of their π -electron energies. By further developing the discussion, we search for clues to realize stacked aromaticity in synthesizable molecular systems.

Introduction

Aromaticity is one of the core concepts of organic chemistry,¹ which has long fascinated not only organic chemists but also theoretical chemists, especially those involved in chemical graph theory.^{2,3,4,5} As shown in Figure 1, the adjacency matrix describing the topology of the network of π electrons is equivalent to the Hückel matrix, and the eigenspectrum of the graph allows us to evaluate the energy of the π electron system. The stability of aromatic compounds and the instability of antiaromatic compounds can be discussed

primarily on the basis of the π -electron energy obtained with the Hückel method.⁶ Such a correspondence between graph theory and the Hückel method inspires attempts to understand aromaticity in graph-theoretic ways.^{7,8} To conduct a more precise discussion, attention should be paid not only to the properties of π electrons but also to those of σ electrons. It should be noted that Pierrefixe and Bickelhaupt⁹ have shown that the propensity of the π electrons in cyclobutadiene as well as in benzene is always to localize the double bonds, against the delocalizing force of the σ electrons. More importantly, they have also shown that the π electrons nevertheless decide about the localization or delocalization of the double bonds.

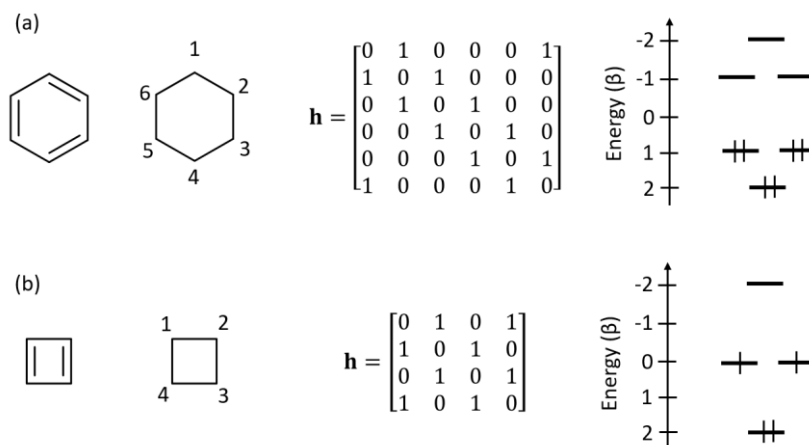


Figure 1. Application of Hückel molecular orbital method to (a) benzene and (b) cyclobutadiene. \mathbf{h} represents the adjacency matrix or Hückel matrix. β represents the resonance integral between the 2p orbitals of adjacent carbon atoms.

Aromaticity is a concept applicable to planar cyclic π -conjugated systems, but the scope of its application has continued to expand: σ -aromaticity,¹⁰ Möbius aromaticity,¹¹ spherical aromaticity,¹² and three-dimensional aromaticity^{13,14} have been added to the list. Such an extension of the notion of aromaticity has led to an extension of the scope of chemical graph theory.^{15,16} Chemistry stimulates mathematics, and mathematics stimulates chemistry back. In recent years, yet another aromaticity concept, stacked aromaticity or stacked-ring aromaticity and its opposite, stacked antiaromaticity, have begun to attract attention.^{17,18,19}

In 2007, Corminboeuf, Schleyer, and Warner proposed, based on density functional theory (DFT) calculations, that when two antiaromatic rings are stacked, e.g., a methano-bridged superphane composed of a cyclobutadiene dimer (**1** in Figure 2), the antiaromaticity disappears due to stacked aromaticity caused by the interaction between the frontier orbitals of each π system.²⁰ Their work sparked the recent boom in research on stacked aromaticity. Bean and Fowler analyzed stacked aromaticity in terms of ring currents,²¹ and Aihara analyzed it in terms of graph theory.²² We analyzed it in terms of frontier orbital interactions.²³

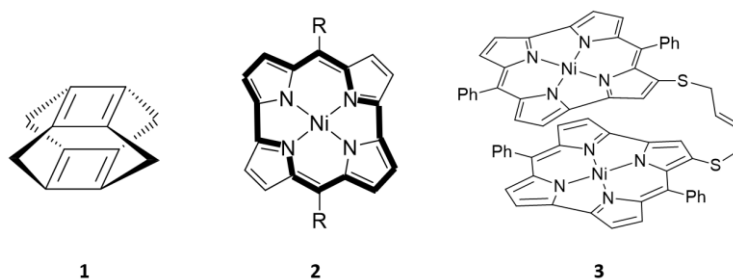


Figure 2. Molecular structures of cyclobutadiene superphane (**1**), norcorrole Ni(II) (**2**), and stacked norcorrole dimer (**3**). The 16 π -electronic circuit in **2** is indicated by the bold line.

Frenking and co-workers²⁴ made the following claim: Aromatic compounds exhibit magnetically induced ring current, but the reverse conclusion that sustaining magnetically induced ring current identifies aromaticity is not justified. This is a highly significant observation because it implies that the calculation or measurement of magnetic indices, i.e. NICS or current density, is not a reliable method to ascertain the aromatic character of a molecule. Stacked aromaticity has been characterized primarily on the basis of magnetic indices.^{20,21} However, energy- and geometry-based indices such as topological resonance energy²² and the harmonic oscillator model of aromaticity¹⁸ have also been used for the characterization of stacked aromaticity. The fact that stacked aromaticity has been characterized by such a variety of indices would justify the labeling of it as a form of aromaticity.

It should be noted that aromaticity is synonymous for a particular stability of cyclic delocalized systems.²⁴ In other words, the most fundamental attribute of aromatic compounds is their energetic stability with regard to reference compounds. Stabilization of antiaromatic rings by close face-to-face π -stacking may be traced back to experimental observations in the 1970s on the syn dimerization of cyclobutadiene.^{25,26} We also note that there was an interesting discussion on the topic made by Woodward and Hoffmann in the 1960s.²⁷ Although the term “stacked aromaticity” did not exist, from a modern perspective it implied stacked aromaticity. The earliest such studies were summarized by Greenberg and Liebman in 1978 in a section of their book.²⁸ Stacking and dimerization of cyclobutadiene, pentalene, and other antiaromatic rings, have been investigated theoretically.^{29, 30, 31} Tracing its history coincides not only with tracing the development of computational methods, but also with tracing the development of attempts to theoretically define what aromaticity is.

We need to respect the efforts of synthetic chemists who have tried to break the status quo where substances exhibiting stacked aromaticity were presumed to exist as ephemeral intermediates beyond observation or exist only in computers.^{32,33,34,35} Many of their efforts yielded different results than they had hoped. Eventually, in 2016, Shinokubo and his collaborators published their work on the stacking structure of a contracted porphyrin analogue called norcorrole (**2** in Figure 2), which exhibits 16 π antiaromaticity.³⁶ The synthesis of closely stacked antiaromatic π -conjugated systems has been achieved for the first time using norcorrole Ni(II) complexes (**3** in Figure 2). In the stacked norcorrole, a significant reduction of antiaromaticity and the emergence of aromatic features, such as improved stability, homogenized bond lengths, and effective electron delocalization were observed.³⁶ Shinokubo’s group subsequently succeeded

in synthesizing a cyclophane of norcorrole,³⁷ and furthermore, not only observed the stacking structure of norcorrole in the liquid and solid phases,³⁶ but also succeeded in forming the stacking structure in a supramolecular micellar capsule.³⁸

In this study, we use the Hückel method to derive a closed form expression for the stacked system and discuss the origin of the stabilization associated with the coupling of two cyclobutadiene rings to a face-to-face stacked dimer based on the energy of the π -electron system. At the same time, we discuss the fact that such stabilization does not occur when two benzene rings are combined into a face-to-face stacked dimer. As a result, the mathematical aspect that the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of the monomer is an important factor determining whether the system is stabilized or not is revealed. On this basis, we seek to understand the characteristics of stacked aromaticity and stacked antiaromaticity. It will be shown that the findings obtained are generalizable and that norcorrole, a molecule showing stacked aromaticity that has actually been synthesized, can be discussed within the framework of our Hückel model. This implies that experimental chemists will be able to design molecules exhibiting stacked aromaticity easily using the Hückel method. We believe that the above is a novelty of this study.

Results and Discussion

Schematic illustrations of the dimer of benzene and that of cyclobutadiene in a close face-to-face stacking structure are shown in Figure 3a and 3b, respectively. This figure also shows the Hückel matrices (adjacency matrices) for these structures. Although these matrices are large in size, they can be simplified as block matrices as suggested by the dashed lines in the figure. With the Hückel matrix of the monomer as \mathbf{h} and the unit matrix as \mathbf{I} , the Hückel matrix of the dimer can be written as

$$\mathbf{H} = \begin{bmatrix} \mathbf{h} & t\mathbf{I} \\ t\mathbf{I} & \mathbf{h} \end{bmatrix}. \quad (1)$$

where t is a parameter that describes the strength of the through-space p-p σ -type interaction between the 2p orbitals of the carbon atoms due to stacking. We will denote the characteristic polynomial of \mathbf{H} as $p_{\mathbf{H}}(\lambda) = \det(\mathbf{H} - \lambda\mathbf{I})$. The roots of the equation $p_{\mathbf{H}}(\lambda) = 0$ are the eigenvalues of \mathbf{H} . Since \mathbf{H} is a block matrix as in eq. 1, $p_{\mathbf{H}}(\lambda)$ can be expressed as a block matrix determinant as follows:

$$p_{\mathbf{H}}(\lambda) = \det \begin{bmatrix} \mathbf{h}' & t\mathbf{I} \\ t\mathbf{I} & \mathbf{h}' \end{bmatrix}, \quad (2)$$

where $\mathbf{h}' = \mathbf{h} - \lambda\mathbf{I}$. \mathbf{h}' is the monomer's Hückel matrix with all diagonal components replaced by $-\lambda$. Figure 1 shows the eigenspectra of the monomers, and the operation here corresponds to shifting the origin of the energy of those spectra to $-\lambda$.

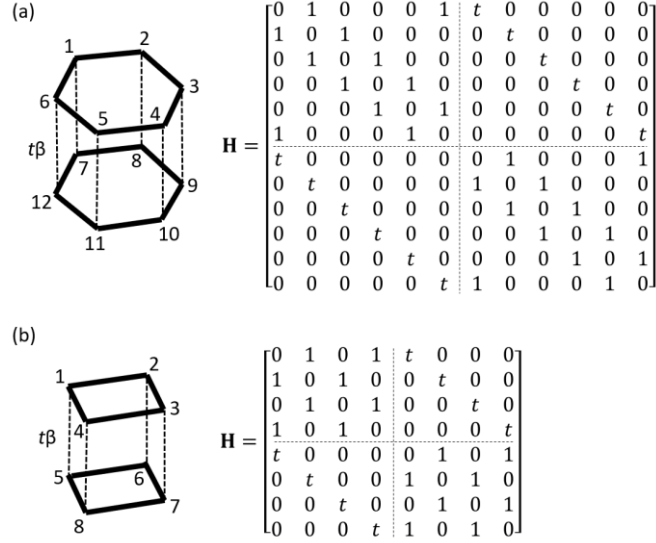


Figure 3. Schematics of the close face-to-face stacking structures of (a) benzene and (b) cyclobutadiene dimers and the Hückel matrices (adjacency matrices) for them. Let $t\beta$ be the resonance integral for the through-space p-p σ -type interaction between the 2p orbitals of the carbon atoms stacked.

As shown in Figure 1b, the square cyclobutadiene molecule has nonbonding molecular orbitals (NBMOs) with energy eigenvalues of 0, so \mathbf{h} of cyclobutadiene is not invertible. The shift in energy due to the introduction of $-\lambda$ has made \mathbf{h}' invertible. Eq. 2 can be transformed as follows:

$$p_{\mathbf{H}}(\lambda) = \det(\mathbf{h}')\det(\mathbf{h}' - t^2\mathbf{h}'^{-1}). \quad (3)$$

Here we have used a useful formula, $\det \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{bmatrix} = \det(\mathbf{A})\det(\mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B})$.^{39,40,41} There is also another useful formula, $\det(\mathbf{A})\det(\mathbf{B}) = \det(\mathbf{A}\mathbf{B})$.⁴² Using this, eq. 3 can be transformed as follows:

$$p_{\mathbf{H}}(\lambda) = \det(\mathbf{h}'^2 - t^2\mathbf{I}). \quad (4)$$

Interestingly, this is the characteristic polynomial for the eigenvalue problem of

$$\mathbf{h}'^2\mathbf{x} = t^2\mathbf{x}. \quad (5)$$

The time-independent Schrödinger equation for the Hückel matrix \mathbf{h} , which can be viewed as the Hamiltonian of the monomer, can be written as⁴³

$$\hat{h}\vec{\psi}_j(\mathbf{r}) = E_j\vec{\psi}_j(\mathbf{r}). \quad (6)$$

That for \mathbf{h}' can be written as

$$\hat{h}'\vec{\psi}_j(\mathbf{r}) = (E_j - \lambda)\vec{\psi}_j(\mathbf{r}). \quad (7)$$

Thus, if \mathbf{h}'^2 is regarded as a Hamiltonian matrix, the Schrödinger equation for it can be written as

$$\hat{h}'^2\vec{\psi}_j(\mathbf{r}) = (E_j - \lambda)^2\vec{\psi}_j(\mathbf{r}). \quad (8)$$

Since eq. 5 and eq. 8 are essentially equivalent, we obtain

$$t^2 = (E_j - \lambda)^2. \quad (9)$$

This can be transformed into

$$\lambda = E_j \pm t. \quad (10)$$

Note that λ is an eigenvalue for the dimer Hamiltonian while E_j is that for the monomer's.

It is meaningful to get an idea of what value t takes in realistic π - π stacking compounds. Figure 4 shows a graph plotting t as a function of stacking distance. This graph is based on Mulliken et al.'s study⁴⁴ and is a reproduction of one we previously prepared.⁴⁵ Typical π - π stacking distances range from 3.3 to 3.8 Å.⁴⁶ The stacking distance between antiaromatic rings is much shorter. The stacking distance of the norcorrole complexes observed by Shinokubo and co-workers is about 3.1 Å.^{36,37} Note that norcorrole molecules have been observed to be stacked with an interlayer distance smaller than that of bilayer graphene (3.4 Å).⁴⁷ This is surprising given that the dispersion energy between perfectly planar and almost infinitely spread graphene sheets is much greater. The key to understanding this is to realize that the interaction between norcorrole molecules is not governed solely by dispersion forces.¹⁸ The stacking distance in cyclobutadiene superphane (**1**) optimized by Corminboeuf et al. is as short as about 2.1 Å.²⁰ Consider the case where the stacking distance is 2.1 Å or greater. In that case, t takes values in the range $-0.9 \leq t \leq 0$.

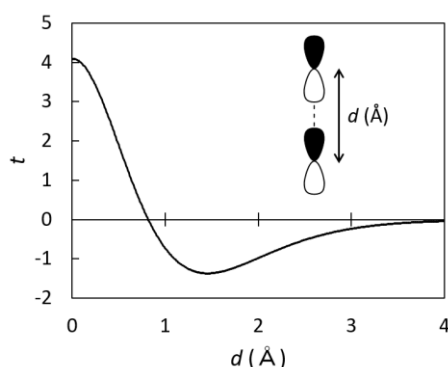


Figure 4. Resonance integral for the through-space p-p σ -type interaction between the 2p orbitals of the carbon atoms stacked is plotted as a function of the stacking distance d , with the unit on the vertical axis being β .

A diagram depicting the correlation between the orbital levels of the monomer and those of the dimer, considering the range of possible values of t , is shown in Figure 5. This figure is a graphic representation of what eq. 10 means. Moving from the monomer to the dimer, one can see the orbital splitting into two. One may call such an orbital splitting the Davydov splitting.^{35,48}

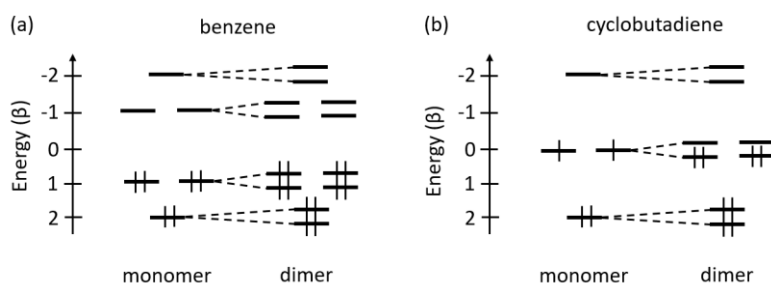


Figure 5. Correlation diagrams between the monomer and dimer orbitals of (a) benzene and (b) cyclobutadiene.

Figure 5 shows that there are two patterns of splitting of occupied orbitals: one is the splitting of doubly occupied orbitals and the other is that of singly-occupied orbitals (compared in Figure 6). In the splitting of doubly occupied orbitals, the stabilization and destabilization of the orbital cancel each other out. On the other hand, in the splitting of singly occupied orbitals, the system only enjoys stabilization. As such, benzene does not have the driving force to dimerize, but cyclobutadiene does. This is probably the simplest explanation for the face-to-face stacking of two benzene rings leading to stacked antiaromaticity while that of cyclobutadiene leading to stacked aromaticity.

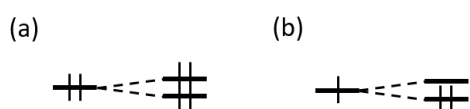


Figure 6. (a) Splitting of a doubly occupied orbital and (b) that of a singly occupied orbital.

The stabilization of a system by the splitting of singly occupied orbitals is also used to describe the formation of pancake bonding.^{49,50,51} Stabilization by interaction between singly occupied molecular orbitals (SOMOs) is well known as the driving force for radical dimerization.^{52,53} Although the Lewis structure of cyclobutadiene has no unpaired electrons, the energy level diagram shown in Figure 1b indicates that it is a definite diradical(oid).⁵⁴ Exploring the relationship between pancake bonding and stacked aromaticity will be an interesting future challenge. One of the anonymous reviewers of this paper made a very interesting suggestion about this: Pancake bonding and stacked aromaticity appear to be single and double bonded versions of face-to-face (covalent) bonding between two π -conjugated polycyclic species that are, respectively, a mono-radical and a triplet diradical (the latter being $4n\pi$ electron Baird aromatic⁵⁵). That is, the structure with stacked aromaticity occurs as a (formal) combination of two Baird aromatic triplet annulenes (one annulene has two unpaired $\pi(\alpha)$ electrons and the other has two unpaired $\pi(\beta)$ electrons). The stacked aromatic interaction may be called a double pancake bond. The reviewer's suggestion is plausible in terms of bond orders based on orbital interactions and we fully agree with it. However, we have calculated the Wiberg bond index between two cyclobutadiene rings forming a face-to-face bond in a previous study²³ and found it to be approximately 1, indicating the presence of a single-bond interaction. This still means that further investigation of the relationship between pancake bonding and stacked aromaticity is needed.

Figure 7 shows the energy level diagram of norcorrole calculated with the Hückel method. The structure of norcorrole depends on the type of the central metal ion as well as its presence or absence; metal-free norcorrole and Ni(II) norcorrole (Figure 2) do not have a perfectly planar structure.⁵⁶ Here, however, a perfectly flat structure was assumed for computational convenience. The energy gap between the HOMO and the LUMO is very small, $0.31|\beta|$. Thus, this molecule may involve diradical character to some extent, but it is not as obvious a diradical as cyclobutadiene. Actually, the diradical character of norcorrole determined by using the unrestricted Hartree-Fock method^{57, 58} is 0.65. Nevertheless, norcorrole is kinetically persistent,⁵⁹ while cyclobutadiene is not. The origin of norcorrole forming close face-to-face π -

stacking stabilized by stacked aromaticity is not the SOMO-SOMO interaction. The stabilization mechanism involving the HOMO and LUMO that we proposed in our prior paper plays an important role.²³

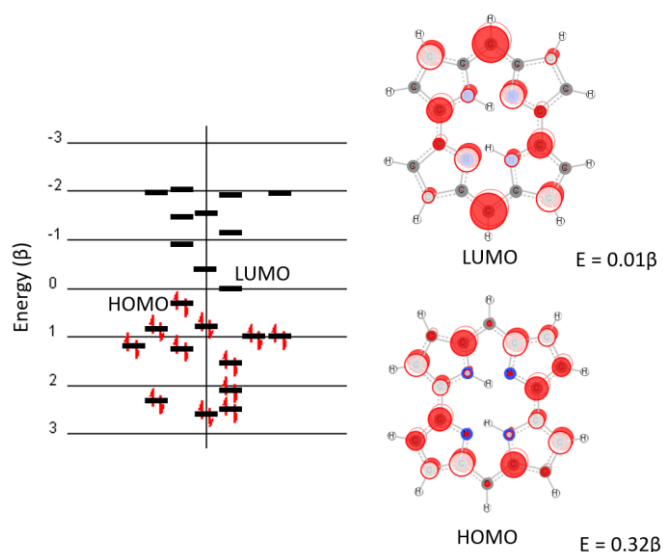


Figure 7. Energy level diagram (left) and HOMO and LUMO distributions (right) of norcorrole calculated using the Hückel method.

As depicted in Figure 8a, the orbital splitting of the HOMO results in an orbital having a lower energy by $|t|$ compared to the energy of the monomer's HOMO. This orbital is occupied by two electrons, leading to an energy reduction of $2|t|$. On the other hand, the energy of the other orbital is raised by $|t|$ relative to the monomer's HOMO energy. This orbital is also occupied by two electrons, which offsets the energy reduction. In other words, the orbital energy changes due to the HOMO splitting exactly balance out. As shown in Figure 8b, when the HOMO-LUMO gap of the monomer is exactly $2|t|$, the higher energy orbital resulting from the HOMO splitting and the lower energy orbital resulting from the LUMO splitting become degenerate. In Figure 8c, when the HOMO-LUMO gap of the monomer is smaller than $2|t|$, the energy of the lower orbital resulting from the LUMO splitting becomes lower than the energy of the higher orbital resulting from the HOMO splitting. Consequently, the former orbital is occupied by two electrons while the latter is unoccupied. If the HOMO-LUMO gap of the monomer is smaller than $2|t|$ but greater than $|t|$, the energy of the lower orbital resulting from the LUMO splitting is higher than the monomer's HOMO energy. However, the energy difference between these two orbitals is smaller than $|t|$. Therefore, the energy difference is insufficient to completely offset the energy reduction from the lower orbital produced by the HOMO splitting. In other words, the system begins to undergo stabilization when the HOMO-LUMO gap of the monomer gets smaller than $2|t|$. Such a stabilization process involves a charge transfer from the HOMO to the LUMO. A similar process can be seen in hydrogen under pressure, which was thoroughly investigated by Hoffmann and co-workers.^{60,61,62,63}

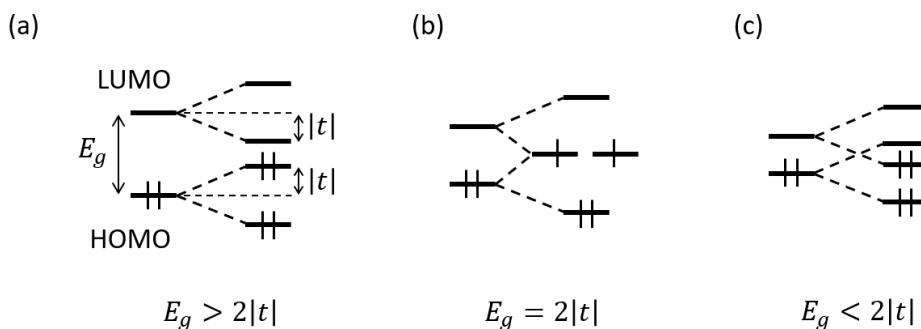


Figure 8. How the occupancy of the orbitals generated by the HOMO and LUMO splitting of the monomer changes as the HOMO-LUMO gap (E_g) of the monomer becomes smaller: (a) $E_g > 2|t|$, (b) $E_g = 2|t|$, and (c) $E_g < 2|t|$.

From the above discussion, we can conclude that the property of stacked aromaticity emerges when the HOMO-LUMO gap of the monomer is less than $2|t|$. From Figure 4, $|t|$ is at most 1.0 within the range of realistic stacking distances. This means that molecules with a HOMO-LUMO gap greater than 2.0 in the unit of $|\beta|$ do not exhibit stacked aromaticity.

From Figure 7, the HOMO-LUMO gap of norcorrole is 0.31 in the unit of $|\beta|$. Based on Figure 4, the stacking distance would have to be about 3.2 Å or less to maintain $2|t| \geq 0.31$. Indeed, the experimentally observed face-to-face stacking distance for a norcorrole dimer whose stacking cores are almost overlapped is 3.258 Å.¹⁸ This indicates that there is a connection between the predictions made by the qualitative model presented in this paper and the experimental data for known systems, thus demonstrating the validity of our model. The relationship between the HOMO-LUMO gap (in $|\beta|$) of a monomer and the stacking distance at which it begins to exhibit stacked aromaticity is shown in Figure 9. The reader may find this plot useful in designing new stacked aromatic compounds.

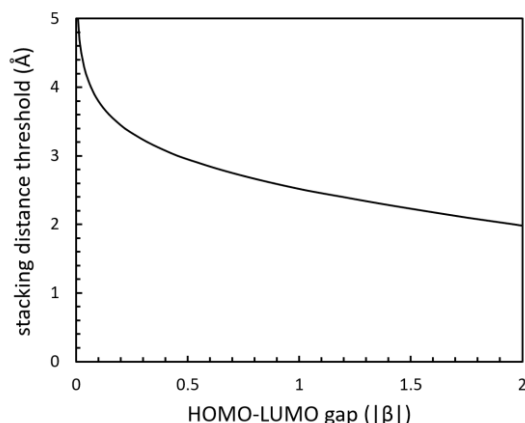


Figure 9. Relationship between the HOMO-LUMO gap of a monomer (in the unit of $|\beta|$) and the stacking distance at which it begins to exhibit stacked aromaticity.

From Figure 9, it is expected that if the HOMO-LUMO gap of a monomer is small, stacked aromaticity will develop even if the stacking distance is long. On the other hand, if the HOMO-LUMO gap is large, stacked aromaticity will not be realized. Synthesis of a planar π -conjugated molecule with a small HOMO-LUMO gap is essential for the creation of compounds that exhibit stacked aromaticity. For such a purpose, it would be useful to investigate the origin of the small HOMO-LUMO gap in norcorrole.

To discuss the nature of the small HOMO-LUMO gap of norcorrole, it is better to compare it with that of porphyrin. By removing the methine bridges at the two side meso positions of porphyrin, its π -conjugated structure can be changed to that of norcorrole (see the upper part of Figure 10). Although such a reaction does not actually occur, by plotting the orbital energies as a function of such a conformational change, a diagram can be constructed that correlates the π orbitals of porphyrin with those of norcorrole. This can be regarded as a kind of Walsh diagram.

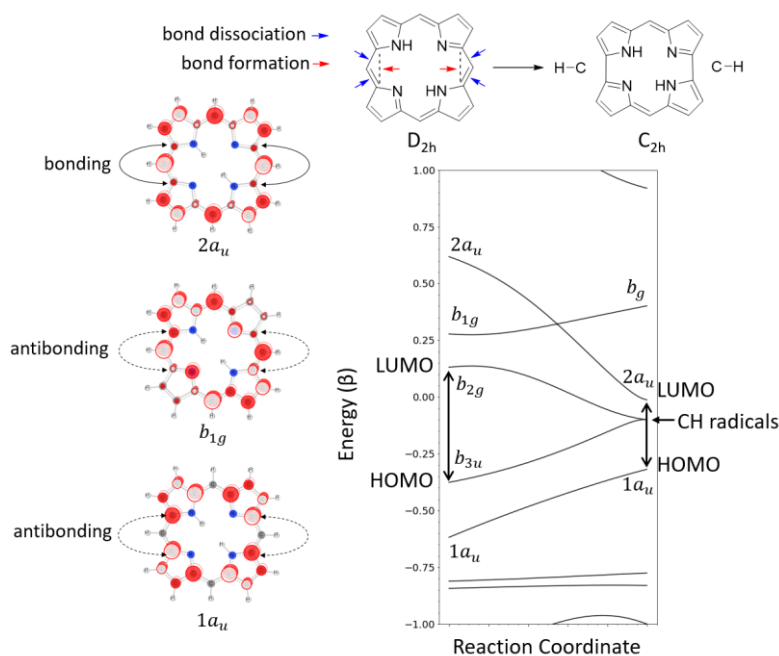


Figure 10. Orbital correlation (Walsh) diagram for a hypothetical transition from porphyrin to norcorrole. These orbital levels were calculated using the Hückel method. By decreasing the absolute values of the resonance integrals for the bonds indicated by the blue arrows in the porphyrin structure and increasing those indicated by the red arrows, a continuous transition from the π orbitals of porphyrin to those of norcorrole is achieved.

The Walsh diagram in Figure 10, which was generated using the Hückel method, shows that the HOMO-LUMO gap for porphyrin with D_{2h} symmetry is defined by the energy difference between the b_{2g} and b_{3u} orbitals and is $0.51|\beta|$. These orbitals transition to the π orbitals of the CH radicals. Their energies should coincide with $E = 0$ because the usual Hückel method takes the value of the Coulomb integral of carbon to be 0. However, the LUMO level of norcorrole is right there and could make the diagram difficult to see, so by perturbing the Coulomb integral of the carbon atoms of the CH radicals, we shifted their energy

levels slightly away from $E = 0$.

Norcorrole usually does not take a completely planar structure, but here, for simplicity, a C_{2h} planar structure was assumed and the symmetry species of its point group was used to label the orbitals. The HOMO-LUMO gap of norcorrole is defined by the energy difference between the two a_u orbitals. These two a_u orbitals are derived from those of porphyrin. Figure 10 also shows the distribution of the $1a_u$ and $2a_u$ orbitals of porphyrin: for the $1a_u$ orbital, there are antibonding orbital interactions as indicated by the dashed arrows; for the $2a_u$ orbital, there are bonding orbital interactions as indicated by the solid arrows. Thus, in the transition from porphyrin to norcorrole, the $1a_u$ orbital is destabilized and the $2a_u$ orbital is stabilized. Looking at the unoccupied region of porphyrin, there is an orbital that is closer to the frontier region than the $2a_u$ orbital. It is the b_{1g} orbital. However, it moves away from the frontier region due to the antibonding interactions indicated by the dashed arrows.

From the above observation we can learn the following. In the unoccupied region, there is a molecular orbital with an in-phase relationship around the contraction part, while in the occupied region, there is a molecular orbital with an out-of-phase relationship around the contraction part, and so they encroach into the frontier region with contraction. Molecular orbitals with out-of-phase relationship around the contraction part in the unoccupied region and those with in-phase relationship around the contraction part in the occupied region may also exist but they will move away from the frontier region as the transition from porphyrin to norcorrole. Therefore, there is no need to be concerned with them. Since aromatic compounds usually have a large HOMO-LUMO gap,⁶⁴ the orbitals encroaching into the frontier region will often result in a decrease in the HOMO-LUMO gap.

The relationship between porphyrin and norcorrole, seen above, is similar to that between benzene and cyclobutadiene. As shown in Figure 1b, cyclobutadiene has NBMOs and no clear HOMO-LUMO gap can be defined for it. However, D_{4h} cyclobutadiene shown in Figure 1b is transformed to that of D_{2h} by a second-order Jahn-Teller distortion.^{65,66} The D_{2h} cyclobutadiene has a bond alternation and a small HOMO-LUMO gap. It can then be reproduced using the Hückel method, which involves perturbations to the resonance integrals of the C-C bonds.⁶⁷ Figure 11 shows a Walsh diagram of the correlation between the π orbitals of benzene and D_{2h} cyclobutadiene, obtained using the same technique as in Figure 10. There are two types of orbitals: those that move away from the frontier region and those that encroach into the frontier region. Therefore, the HOMO-LUMO gap is still reduced by ring contraction.

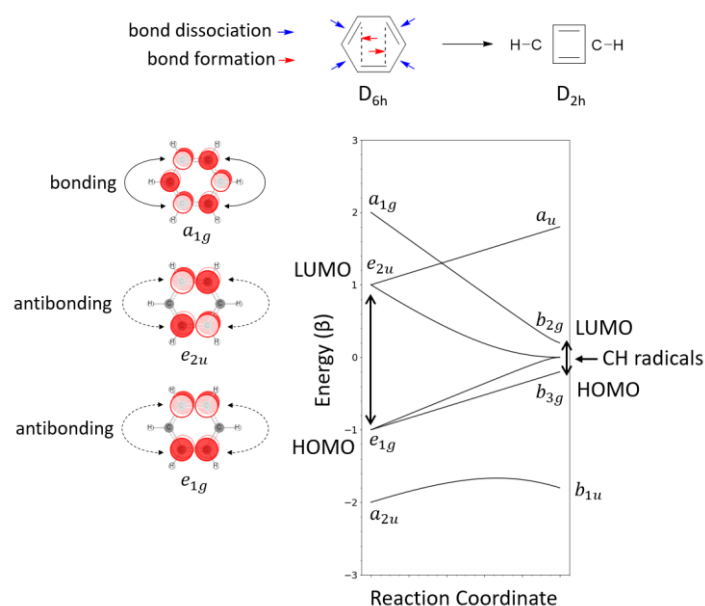


Figure 11. Orbital correlation (Walsh) diagram for a hypothetical transition from benzene to D_{2h} cyclobutadiene. These orbital levels were calculated using the Hückel method. By decreasing the absolute values of the resonance integrals for the bonds indicated by the blue arrows in the benzene structure and increasing those indicated by the red arrows, a continuous transition from the π orbitals of benzene to those of cyclobutadiene is achieved.

Along with ring contraction, the introduction of heteroatoms is also an important concept for the formation of antiaromatic porphyrin analogues: 5,15-dioxaporphyrin **4** is an example, shown in Figure 12. Each O atom at the two side meso positions provides two π -electrons for the π -system, thus a 20π -electron conjugated system formed.⁶⁸ However, it has been suggested that this π -conjugated molecule does not exhibit stacked aromaticity.³⁵ The reason for this may be that the HOMO-LUMO gap of this molecule is not so small as discussed in the Supporting Information (SI) to this paper.

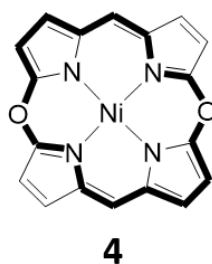


Figure 12. Molecular structure of 5,15-dioxaporphyrin (**4**). The 20π -electronic circuit is indicated by the bold line.

Based on the discussion up to this point, it is clear that ring contraction is the most plausible method for creating molecules that exhibit stacked aromaticity. Therefore, we focus on ring contraction to present a more realistic molecule that could be synthesized as a candidate for a stacked aromaticity molecule. As

shown in Figure 13a, phthalocyanine (**5**) is an aromatic molecule characterized by its 18π electronic circuit.⁶⁹ The ring-contracted analogue of this molecule (**6**) is shown in Figure 13b. The energy level diagrams calculated for these molecules are shown in Figure 14. The HOMO-LUMO gap of **5** is $0.39|\beta|$ while that of **6** is $0.16|\beta|$. We did a literature search and could not find any information on the synthesis of **6**. However, the synthesis of such a molecule would not be far-fetched, given that norcorrole, a contracted ring analogue of porphyrin, has been synthesized. Looking at Figure 9 with the relatively small HOMO-LUMO gap of $0.16|\beta|$ of this molecule in mind, such a system would be expected to exhibit stacked aromaticity if the stacking distance of the face-to-face stacked dimer of the ring-contracted phthalocyanine molecules can be reduced to 3.5 \AA or less. We have confirmed that this prediction is correct based on DFT calculations. The results are shown in SI.

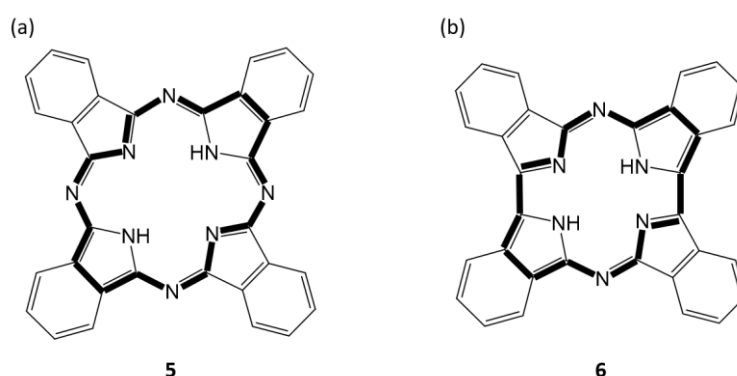


Figure 13. Molecular structures of (a) phthalocyanine (**5**) and (b) its ring-contracted analogue (**6**). The former 18π electronic circuit and the latter 16π electronic circuit are indicated by bold lines.

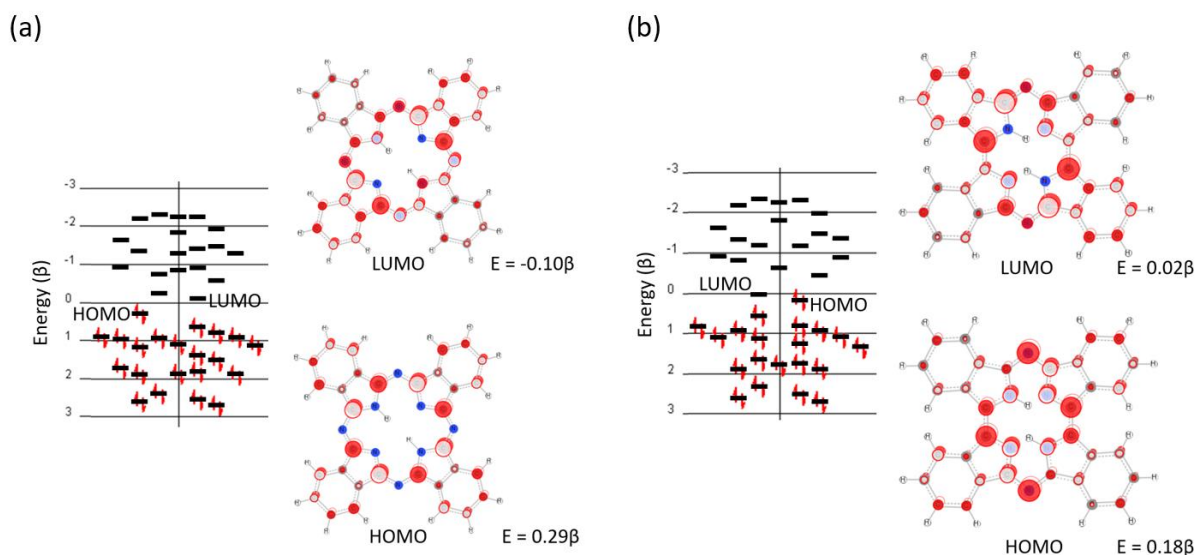


Figure 14. Energy level diagrams (left) and HOMO and LUMO distributions (right) of (a) phthalocyanine and (b) its ring-contracted analogue calculated using the Hückel method.

Up to this point, our discussion has been based on the assumption of a face-to-face π -stacking

structure with completely overlapping stacking cores. We consider stacked structures with two twisted π -planes. In 2019, Shinokubo and co-workers synthesized a norcorrole cyclophane (**7**) shown in Figure 15 and confirmed its stacked aromatic nature.³⁷ In the synthesized cyclophane, two norcorrole units were rotated relative to each other by 22° . The interplanar distance between the two norcorrole planes was 3.09 \AA . In 2021, they further conducted a systematic study of the effect of the twist angle between the two π planes on the emergence of stacked aromaticity.¹⁸ They reported the crystal structures of norcorrole cyclophane with an interplane distance of 3.258 \AA and a twist angle of nearly 0° and that with an interplane distance of 3.33 \AA and a twist angle of 36° . They were both obtained as polymorphs of molecule **8** shown in Figure 15. It was confirmed that the former shows the signatures of stacked aromaticity while the latter does not. Based on the above facts, it can be deduced that the stacked system will no longer exhibit stacked aromaticity when the torsion angle increases to some extent.

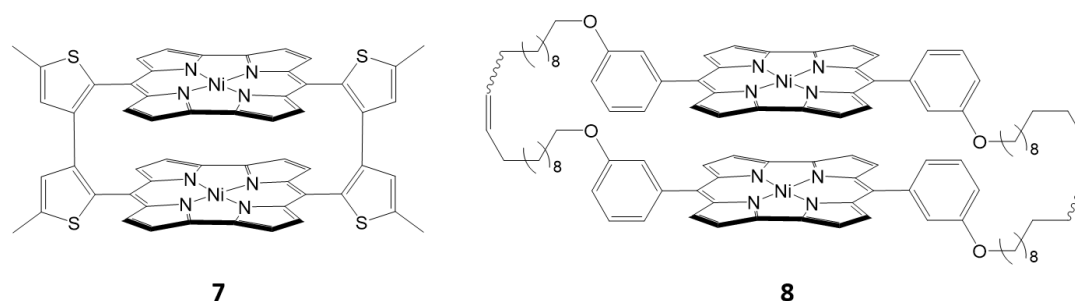


Figure 15. Molecular structures of norcorrole cyclophanes reported in 2019 (**7**)³⁷ and 2021 (**8**).¹⁸

We have seen in Figure 4 how the overlap of the 2p orbitals changes as the distance between the π planes changes. In a similar way, let us see how it changes with the twist between the π planes. Two π -planes stacked at stacking distance d are modeled as two circles of radius r , as shown in Figure 16. In this figure, the magnitude of the torsional angle between these π -planes is θ . Let \mathbf{d} be the normal vector to the π plane and \mathbf{R} be the vector from the lower 2p orbital to the upper 2p orbital. The angle between these two vectors is ϕ . According to Mulliken et al.,⁴⁴ the resonance integral between these two 2p orbitals is written in units of β by the following equation:

$$t(R, \phi) = \frac{S_{\pi\pi}(R)}{S_0} \sin^2 \phi - \frac{S_{\sigma\sigma}(R)}{S_0} \cos^2 \phi, \quad (11)$$

where $S_{\pi\pi}(R)$ and $S_{\sigma\sigma}(R)$ are the distance dependences of the p-p π -type and σ -type overlap integrals, respectively. S_0 is the referential overlap integral, and in the Hückel method for π -conjugated systems, it would be reasonable to set $S_0 = S_{\pi\pi}(R = 1.4 \text{ \AA})$, where 1.4 \AA corresponds to the length of the C-C bonds in benzene.⁴⁵ When considering the interaction between the 2p orbitals of carbon atoms, $S_{\pi\pi}(R)$ and $S_{\sigma\sigma}(R)$ are respectively represented by the following polynomials:⁷⁰

$$S_{\pi\pi}(R) = e^{-p} \left(1 + p + \frac{2}{5}p^2 + \frac{1}{15}p^3 \right), \quad (12)$$

and

$$S_{\sigma\sigma}(R) = e^{-p} \left(-1 - p - \frac{1}{5}p^2 + \frac{2}{15}p^3 + \frac{1}{15}p^4 \right), \quad (13)$$

where $p = \zeta R$ with the orbital exponent ζ for the 2p orbitals of the carbon atom being 3.07 \AA^{-1} .⁷¹ Rewriting eq. 11 using eqs. 12 and 13 yields

$$t = \frac{e^{-p}}{s_0} \left[1 + p + \frac{2}{5}p^2 + \frac{1}{15}p^3 - \frac{1}{5} \left(p^2 + p^3 + \frac{1}{3}p^4 \right) \cos^2 \phi \right]. \quad (14)$$

Note that $\cos\phi = d/R$ by definition. Using elementary geometry knowledge, we get

$$R = \sqrt{2r^2(1 - \cos\theta) + d^2}. \quad (15)$$

From the above, we see that t is a function of r , θ , and d .

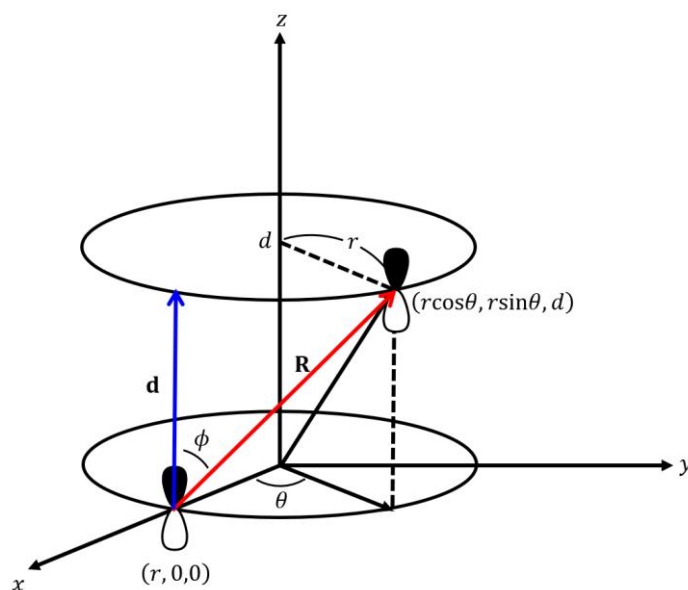


Figure 16. Cylindrical coordinate system for modeling orbital overlap between 2p orbitals spanning two stacked twisted π planes.

As shown using Figure 8c, for a stacked cyclic dimer to exhibit stacked aromaticity, the HOMO-LUMO gap of the monomer must be smaller than $2|t|$. Using the equations derived above, let us see how $2|t|$ changes as the torsion angle θ increases. Figure 17 shows how $2|t|$ varies with increasing θ for the case where the stacking distance d is 3.0 \AA . As θ increases, $2|t|$ decays, so mathematically, increasing θ has the same effect as increasing d . Thus, when torsion angles are taken into account, the stacking distances that begin to show the stacked aromaticity shown in Figure 9 represent their upper limits.

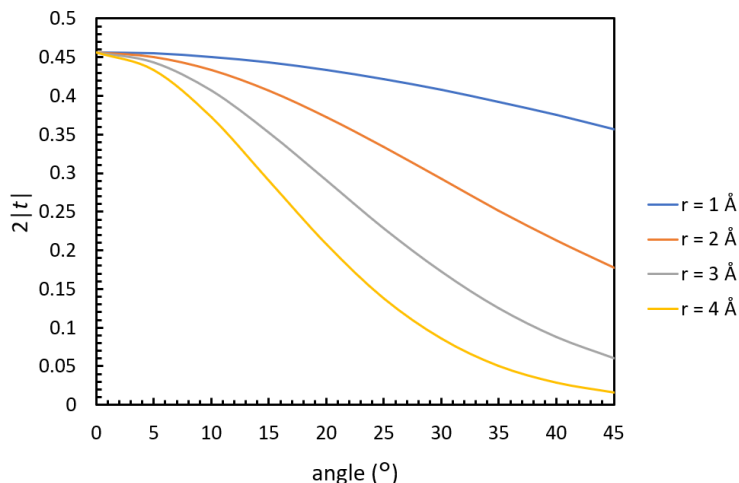


Figure 17. How the double of the absolute value of the resonance integral between 2p orbitals spanning two stacked twisted π planes with the stacking distance of 3.0 Å decays as the size of the torsion angle increases. Shown are the cases of cyclic systems with radii r of 1 Å (blue), 2 Å (orange), 3 Å (gray), and 4 Å (yellow).

In Figure 17, it is worth noting that $2|t|$ decays slowly when θ is small. This suggests that in the limit of small torsional angles, it is possible to make qualitative predictions using the model that assumes a face-to-face type stacking structure as an approximation. It should also be noted that the larger the radius of the cyclic system, the faster $2|t|$ decays with respect to an increase in θ .

Conclusions

Face-to-face stacking of aromatic compounds leads to destabilization; that of antiaromatic compounds leads to stabilization. The former is referred to as stacked antiaromaticity while the latter as stacked aromaticity. Such stabilization and destabilization can be qualitatively reproduced using the Hückel method of calculating π -electron energies. We have considered the π -electron state for the face-to-face stacking structures of benzene and cyclobutadiene within the framework of the Hückel method. The results have shown that the small HOMO-LUMO gap characteristic of the antiaromatic compounds contributes significantly to the stabilization of the system due to stacking. The relationship between the HOMO-LUMO gap of the monomer and the stacking distance for the stabilization of the dimeric face-to-face stacking structure to occur has been clarified. It is also clear that even for antiaromatic compounds, if the HOMO-LUMO gap is not small, stacked aromaticity does not arise unless the stacking structure is formed at fairly close stacking distances. Based on these findings, the π -electronic structure of norcorrole, a candidate compound that exhibits stacked aromaticity was discussed in comparison with that of the parent compound, porphyrin. The electronic structure of a porphyrin derivative was analyzed with the aim of establishing design guidelines for compounds that exhibit stacked aromaticity. It became clear that contracting aromatic rings, as in norcorrole, is a more promising strategy for creating compounds that exhibit stacked aromaticity than the introduction of heteroatoms. Based on the above, we predicted that the ring-contracted analogue of phthalocyanine is a promising molecule that exhibits stacked aromaticity. We further investigated whether

our qualitative Hückel model can be applied to the case where stacked π planes take on a twisted structure with respect to each other. We found that an increase in the torsion angle is mathematically equivalent to an increase in the stacking distance. In other words, we found that the stacking distance must be considerably shorter when designing molecules that exhibit stacked aromaticity in molecular systems with large torsion angles.

Computational Methods

Some of the Hückel calculations were performed using a home-made program, while the others were performed using HuLiS.^{72,73} HuLiS was also used to display the distribution of Hückel molecular orbitals. The heteroatomic parameters used in the Hückel calculations were taken from a reference,⁷⁴ as summarized in Table 1.

Table 1. Parameters for heteroatoms in the Hückel method. The Coulomb integral of a heteroatom and the resonance integral of a bond containing a heteroatom are defined by $\alpha + h\beta$ and $k\beta$, respectively. In this table, the values of h and k are shown. They were obtained from Ref. 74.

heteroatom	h	heteroatomic bond	k
\dot{N}	0.5	C = \dot{N}	1.0
\ddot{N}	1.5	C – \ddot{N}	0.8
\ddot{O}	2.0	C – \ddot{O}	0.8

The diradical character of norcorrole was calculated at the unrestricted Hartree-Fock level with the 6-31G(d,p) basis set implemented in Gaussian 16.⁷⁵ The extended Hückel molecular orbitals shown in Figure S2 were also calculated using Gaussian16. The ring-contracted phthalocyanine analogue shown in SI was calculated at the B3LYP/6-311+G** level using Gaussian16.

ASSOCIATED CONTENT:

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Statement

Supporting Information Analysis of the HOMO-LUMO gap of 5,15-dioxaporphyrin, stacked aromaticity of the face-to-face stacked dimer of the ring-contracted phthalocyanine molecules, and all structural, energy, and vibration analysis data.

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Notes

The authors declare no competing financial interest.

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