

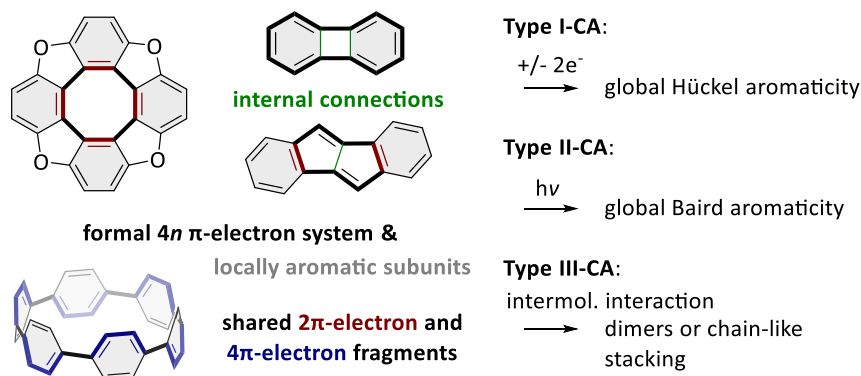
Concealed antiaromaticity

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Abstract: Numerous articles in the recent literature report molecules that are claimed to be antiaromatic, as they feature a formal $4n$ π -electron system. The purported antiaromaticity often serves well as an explanation for some of the observed properties, but it neglects the actual local aromaticity of the molecules, which often feature multiple subunits with $4n+2$ π -electrons besides the formal $4n$ π -electron system. This has led to considerable criticism from those who believe that the term antiaromatic should not be used for any molecule with a formal $4n$ π -electron system but should be reserved for truly antiaromatic molecules. To reconcile the different viewpoints, the term and concept of concealed antiaromaticity is introduced here. The concept accepts that many of the molecules claimed to be antiaromatic are not truly antiaromatic. However, it acknowledges that this does not prevent those molecules from exhibiting behaviour under certain conditions that would normally be expected for antiaromatic molecules, due to the formal, concealed $4n$ π -electron system that characterizes these molecules. Based on the conditions under which the molecules can behave like antiaromatic molecules, three types of concealed antiaromaticity are distinguished here: concealed antiaromaticity revealable in redox reactions (Type I-CA), upon excitation (Type II-CA), and in intermolecular interactions (Type III-CA). The concept of concealed antiaromaticity will enable the conscious, rational design of molecules that show the desirable properties of antiaromatic molecules while avoiding or diminishing the undesirable properties, namely the low stability of truly antiaromatic molecules. This will yield molecules and materials with highly interesting properties for a broad range of applications, from organic electronics to supramolecular chemistry.

Molecules with a cyclic delocalized π -electron system of $4n+2$ π -electrons, where n is a non-negative integer, are aromatic according to Hückel's rule, whereas with $4n$ π -electrons they are antiaromatic.^{1,2} These rules of ground-state aromaticity are reversed in the lowest singlet and triplet excited states, where molecules with a cyclic delocalized system of $4n$ π -electrons are expected to be aromatic and with $4n+2$ π -electrons to be antiaromatic according to what is known as Baird's rule.³⁻⁶ In all cases, the π -electron system has to be planar or close to planar for the π -electron delocalization to occur. While the π -electron delocalization results in energetic stabilization in the case of aromatic molecules (compared to the corresponding localized structure), it leads to destabilization in the case of antiaromatic molecules. The lower stability of antiaromatic molecules can be rationalized by their two degenerate non-bonding singly occupied molecular orbitals (SOMOs) that are higher in energy than the highest occupied molecular orbital (HOMO) of the corresponding localized structure. In contrast, aromatic molecules feature a closed-shell structure with two degenerate bonding HOMOs that are lower in energy. As a consequence, antiaromatic molecules try to escape antiaromaticity in different ways,⁷ often by adopting a more stable non-planar conformation with localized π -electrons (and a closed-shell structure) or by undergoing reactions. For example, cyclooctatetraene adopts a boat-like non-planar conformation to escape antiaromaticity (Figure 1a),⁸ whereas cyclobutadiene is known to dimerize (Figure 1b).⁹

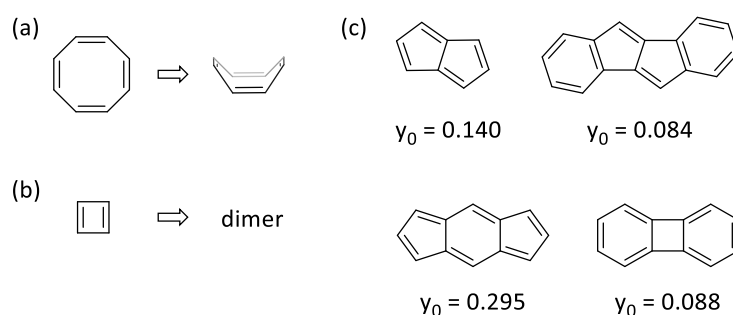


Figure 1. (a) Cyclooctatetraene adopting a non-planar conformation and (b) cyclobutadiene undergoing dimerization to escape antiaromaticity. (c) Molecular structure and diradical character y_0 of pentalene, dibenzopentalene, s-indacene, and biphenylene. The diradical character values are taken from reference 10.

Besides antiaromatic molecules with two degenerate SOMOs and a diradical character y_0 of 1 (referred to as truly antiaromatic molecules in this article), there are molecules with a formal $4n$ π -electron system but reduced diradical character (between 0 and 1).¹⁰ These molecules – including pentalene, dibenzopentalene, s-indacene, and biphenylene (Figure 1c) and their derivatives as well as different cyclooctatetraene derivatives – are often also referred to as antiaromatic,¹¹⁻¹⁸ even when the diradical character is low. However, the classification of such molecules as antiaromatic has been criticized, particularly for polycyclic molecules that feature both formal $4n$ and $4n+2$ π -electron systems (such as dibenzopentalene and biphenylene, Figure 1c right). At the centre of the controversy is the question of whether any molecule with a formal $4n$ π -electron system that exhibits some degree of paratropic current (e.g. in ACID plots or according to slightly shifted NMR signals) can be classified as antiaromatic – a viewpoint often held by experimental organic chemists – or whether the term should be reserved for molecules with a $4n$ π -electron system that fulfil not only the magnetic criterion but also the structural, energetic, and electronic criteria of (anti)aromaticity.^{19,20} While the latter view follows a rather strict holistic approach and is in better

agreement with the definition of (anti)aromaticity, the former is less restrictive and often based on the observation that the molecules in question behave like antiaromatic molecules under certain conditions, which explains why this viewpoint is often held by experimental chemists.

To reconcile the different viewpoints and to enable a rational design of molecules with the observed behaviour, the term and concept of 'concealed antiaromaticity' is introduced here. The concept accepts that many of the molecules claimed to be antiaromatic due to the presence of a formal $4n$ π -electron system are not truly antiaromatic. However, at the same time, it acknowledges that this does not prevent those molecules from exhibiting behaviour under certain conditions that would normally be expected for antiaromatic molecules. Quite the contrary, molecules with concealed antiaromaticity allow the desirable properties of antiaromatic molecules to be used without having to deal with their undesirable properties, namely the low stability of truly antiaromatic molecules.

Molecules with concealed antiaromaticity feature a formal $4n$ π -electron system (Figure 2, bold bonds), but additional structural units and/or conformational changes prevent this $4n$ π -electron system from turning the molecules antiaromatic. In other words, the additional structural units and the conformational changes conceal the antiaromaticity of the molecules. Two effective strategies for concealing the antiaromaticity by structural units have been identified, both integrating fragments of the $4n$ π -electron system into locally aromatic subunits with $4n+2$ π -electrons (Figure 2, grey shadings):

- **Integrating 2π -electron fragments into locally aromatic units** (Figure 2a): This strategy can be regarded as *ortho*-fusing locally aromatic units with the $4n$ π -electron system. Numerous molecules that conceal their antiaromaticity in this way have been reported, ranging from comparatively small molecules like dibenzocyclooctatetraene and tetraoxa[8]circulene (Figure 2a top) to large molecular propellers (Figure 2a bottom).^{16,21,22} In these molecules, the formal $4n$ π -electron system and each of the locally aromatic units share 2 π -electrons.
- **Integrating 4π -electron fragments into locally aromatic units** (Figure 2b): This strategy can be regarded as creating locally aromatic units along the $4n$ π -electron system by introducing 2π -electron bridges. Conjugated macrocycles often conceal their antiaromaticity in this way, including paracyclophanetetraene (Figure 2b top) and cycloparaphenylenes (Figure 2b bottom).²³⁻²⁵ In these macrocycles, the formal $4n$ π -electron system and each of the locally aromatic units share 4 π -electrons.

Both strategies are often assisted by the ability of the $4n$ π -electron system to further conceal the antiaromaticity by conformational changes, unless structural restrictions prevent the $4n$ π -electron system from adopting a non-planar conformation. A combination of different strategies is possible, as can be seen in the macrocycles with phenylene and quinoxaline units in Figure 2c,^{26,27} and often required for a third strategy that has been identified:

- **Connecting the $4n$ π -electron system internally** (Figure 2d): Introducing covalent bonds that connect atoms of the $4n$ π -electron system directly, so without an additional structural unit, can conceal the antiaromaticity / reduce the diradical character.¹⁰ This can be an effective strategy if it leads to the creation of locally aromatic units in which all π -electrons of the locally aromatic units also form part of the formal $4n$ π -electron system, as in biphenylene (Figure 2d top). However, connecting the $4n$ π -electron system internally can considerably reduce the ability of the molecules to further conceal the antiaromaticity by conformational changes. Therefore, this strategy often requires a combination of strategies (especially when the internal connection does not lead to the creation locally aromatic units), as observed in

dibenzopentalene (Figure 2d bottom). As no additional structural units are introduced using this third strategy, it offers less flexibility in terms of molecular design than the other two strategies.

Introducing substituents at the $4n$ π -electron system or heteroatoms in the $4n$ π -electron system can also have an impact on the level of concealment, but these modifications normally need to be combined with one or more of the strategies outlined above. For example, Ni(II) norcorrole features two nitrogen atoms in the formal $4n$ π -electron system, two locally aromatic subunits that integrate $4n$ -electron fragments of the formal $4n$ π -electron system, as well as two vinylene substituents that bridge the π -electron system but do not create locally aromatic units (Figure 2e). The substitution of carbon atoms in the $4n$ π -electron system with nitrogen atoms, as in Ni(II) norcorroles and as studied computationally for pentalene,²⁸ is considered to add to the level of concealment.

While the molecular design strategies outlined above can certainly help to design molecules with concealed antiaromaticity, it should be noted that they may be oversimplifying in some cases: For Ni(II) norcorrole, computations suggest that an aromatic “halo” around the antiaromatic core may contribute to its stability.²⁹ The computations also indicate that the actual delocalization pathway may differ from the formal $4n$ π -electron system in this molecule.

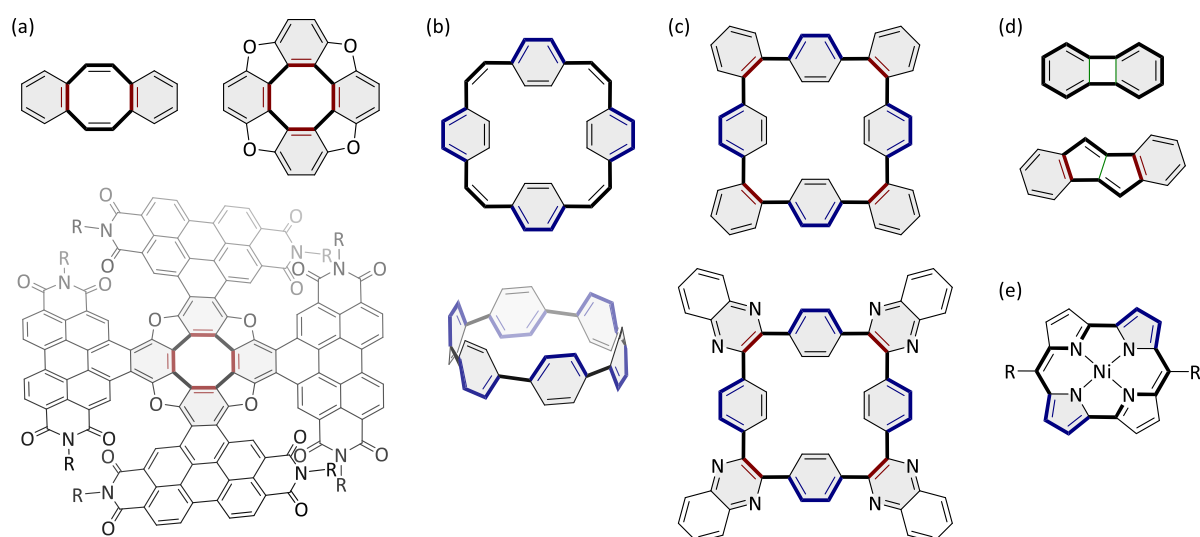


Figure 2. Molecules with concealed antiaromaticity featuring a formal $4n$ π -electron system (bold bonds) as well as locally aromatic subunits with $4n+2$ π -electrons (grey shadings). The locally aromatic subunits share (a) 2π -electron fragments (red) or (b) 4π -electron fragments (blue) with the formal $4n$ π -electron system or (c) both. (d) Molecules with internal connections of the formal $4n$ π -electron system (green). (e) Ni(II) norcorrole featuring substituents at the formal $4n$ π -electron system and nitrogen atoms in the $4n$ π -electron system.

Concealing the antiaromaticity increases the stability of the molecules during synthesis, purification, and processing while retaining desirable properties of antiaromatic molecules, but this depends on how strongly the antiaromaticity is concealed. The integration of fragments of the $4n$ π -electron system into locally aromatic subunits is considered to lead to a tug-of-war between the local aromaticity of the subunits and the global antiaromaticity of the $4n$ π -electron system, which can be influenced by (i) the choice of subunits and the strength of their local aromaticity, (ii) the number of aromatic subunits in relation to the number of π -electrons in the $4n$ π -electron system, and (iii) the ability or disability of the $4n$ π -electron system to undergo conformational changes. Depending on

these factors, different degrees of concealment can be achieved. The antiaromaticity can be strongly concealed like in cycloparaphenylenes (Figure 2b bottom), which feature a high number of strongly aromatic subunits in relation to the number of π -electrons in the formal $4n$ π -electron system, or very weakly concealed like in Ni(II) norcorroles (Figure 2e), which cannot undergo conformational changes due to structural restrictions and only features two locally aromatic subunits in the formal 16 π -electron system, resulting in a relatively high diradical character y_0 of 0.127.³⁰ The degree of concealment determines the conditions under which the molecules can behave like antiaromatic molecules, so the conditions under which they can reveal their concealed antiaromaticity. Based on these conditions, three types of concealed antiaromaticity are distinguished here:

- **Type I-CA:** Concealed antiaromaticity revealable in redox reactions
- **Type II-CA:** Concealed antiaromaticity revealable upon excitation
- **Type III-CA:** Concealed antiaromaticity revealable in intermolecular interactions

The different types of concealed antiaromaticity are not mutually exclusive. Molecules with Type I-CA will often also feature Type II-CA and vice versa. Molecules with Type III-CA will normally also feature Type I-CA and Type II-CA. The three types of concealed antiaromaticity are discussed in more detail below, along with a selection of examples from the literature.

Concealed antiaromaticity revealable in redox reactions (Type I-CA): Molecules with Type I-CA conceal their antiaromaticity in the neutral state but behave like antiaromatic molecules in the doubly reduced or oxidized state, where – just like truly antiaromatic molecules – the molecules become globally aromatic. This is because the formal $4n$ π -electron system transitions to a $4n+2$ π -electron system upon twofold reduction or oxidation. For molecules that can conceal their antiaromaticity by conformational changes, the reduction/oxidation often goes along with a planarization of the involved π -electron system and a loss of the conformational flexibility. The planarization enhances the π -electron delocalization in the system, which is energetically favourable in the doubly charged, aromatic states. However, the molecules can also become globally aromatic if full planarization is not possible for structural reasons.

Type I-CA is the most frequently found type of concealed antiaromaticity in the literature. There are many reports of molecules that become globally aromatic upon twofold reduction or oxidation without being truly antiaromatic in the neutral state and the examples provided here should not be seen as a complete list of molecules exhibiting such behaviour.

To start with some structurally simple examples, both cyclooctatetraene and dibenzocyclooctatetraene feature Type I-CA, as both molecules planarize and become aromatic upon twofold reduction (Figure 3a).^{21,31,32} Similarly, dibenzopentalene (Figure 2d bottom) becomes globally aromatic upon reduction to the dianion or oxidation to the dication.^{33,34} Tetraoxa[8]circulene (Figure 2a top) and the large molecular propeller based on this structure (Figure 2a bottom) also switch to a globally aromatic state upon reduction.¹⁶ Moving on to larger formal $4n$ π -electron systems, paracyclophanetetraene (Figure 2b top) and its derivatives were shown to become globally aromatic upon two-electron reduction or oxidation,³⁵⁻³⁸ although they cannot fully planarize for steric reasons. Using paracyclophanetetraene, switching between a locally aromatic neutral state (with strongly concealed antiaromaticity) and a globally aromatic charged state (Figure 3b) was introduced as a molecular design concept for organic battery electrode materials.²³ Interestingly, when studying tetraimides with a paracyclophanetetraene substructure, evidence was obtained that further reduction to the tetraanion (resulting again in a $4n$ π -electron systems) can yield Baird aromatic molecules with a triplet ground state.³⁹ Ni(II) norcorrole (Figure 2e) also transitions to a globally

aromatic state, both upon twofold reduction and oxidation, and the effect was used to obtain a bipolar battery electrode material.⁴⁰ However, as the antiaromaticity is only weakly concealed in Ni(II) norcorroles (as discussed above), mesityl substituents were attached to increase the stability by steric protection.

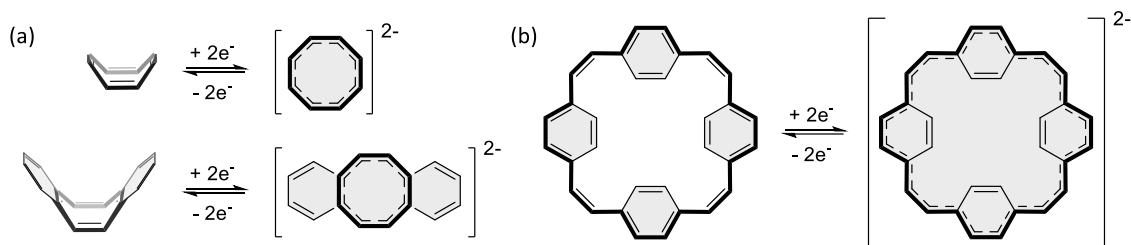


Figure 3. Examples of concealed antiaromaticity revealable in redox reactions (Type I-CA): (a) cyclooctatetraene and dibenzocyclooctatetraene planarize and become aromatic upon twofold reduction, (b) paracyclophanetetraene cannot fully planarize but can still become globally aromatic in redox reactions.

Larger macrocycles, such as cycloparaphenylenes of different size, can also reveal their concealed antiaromaticity in redox reactions, as seen in computational and experimental work.^{24,25,41-43} Each phenylene subunit contributes 4 π -electrons to the formal macrocyclic $4n$ π -electron system, so all cycloparaphenylenes that were studied featured Type I-CA (independent of the number of subunits). In contrast, Gidron et al. recently studied a set of furanylene-acetylene macrocycles in which each of the repeat units contributes 6 π -electrons to the formal macrocyclic π -electron system, resulting in alternation between formal $4n$ and $4n+2$ π -electron systems with increasing ring size.⁴⁴ While the ring currents in the charged state were not studied for these macrocycles, those with a formal $4n$ π -electron system were more readily oxidized in cyclic voltammetry measurements, indicating Type I-CA. For the neutral macrocycles, the authors compared the ring currents to the ring currents in the corresponding phenylene-acetylene macrocycles. Their findings show that the antiaromaticity is more strongly concealed with phenylene than with the furanylene subunits, showing the importance of the strength of the local aromaticity of the subunits. Other examples of macrocycles with Type I-CA include oligofuran macrocycles,^{45,46} expanded carbaisophlorinoids,⁴⁷ heteroatom-substituted porphyrinoids of different size,⁴⁸ and porphyrin-based nanorings.^{49,50}

As was shown for some of the examples here, molecules with Type I-CA can be highly interesting for use as battery electrode materials, as the stability of the charged state and, hence, the reversibility of the redox reaction – common issues of organic battery electrode materials – are increased by the global aromaticity. However, it is envisioned that Type I-CA can also be an interesting feature for electrocatalysis and photoredox catalysis, where it may facilitate charge accumulation.

Concealed antiaromaticity revealable upon excitation (Type II-CA): Molecules with Type II-CA conceal their antiaromaticity in the ground state but behave like antiaromatic molecules in the excited state, where the molecules become Baird aromatic, a behaviour normally ascribed to antiaromatic molecules. As the redox reactions of molecules with Type I-CA, the excitation often goes along with a planarization of the involved π -electron system, but the molecules can also become Baird aromatic if full planarization is not possible for structural reasons.

Many molecules that feature Type I-CA also feature Type II-CA, as shown for cyclooctatetraene, biphenylene, pentalene, and their derivatives.⁵¹⁻⁵⁶ Studies on π -expanded oxepines (Figure 4a) and

other 8π -electron heterocycles with two locally aromatic units fused with the formal 8π -electron system show that these molecules can also feature Type II-CA.⁵⁷⁻⁵⁹ If the antiaromaticity is strongly concealed by fusing a third locally aromatic unit with the formal 8π -electron system, the planarization in the excited state can become sensitive to solvent polarity, temperature, and substituents, as shown for azepine.⁶⁰

Moving on to conjugated macrocycles, paracyclophanetetraene and its derivatives were shown to feature Type II-CA according to computations and experimental indications.³⁷⁻³⁹ Cycloparaphenylenes of different size and their furanylene analogues (Figure 4b) have also been investigated computationally.⁶¹ The results show that – with both types of subunits – the macrocycles can feature Type II-CA. According to most of the computations, the Baird aromaticity was more pronounced in the macrocycles with furanylene units, in which the antiaromaticity is less concealed due to the weaker local aromaticity of the subunits. The authors ascribe this to a tug-of-war between the local Hückel aromaticity of the subunits and the macrocyclic Baird aromaticity in the excited state, which can tip to the favour of macrocyclic Baird aromaticity if weaker locally aromatic subunits are used (or if the number of locally aromatic subunits in relation to number of π -electrons in the macrocyclic π -electron system is reduced) or if steric congestion between the subunits is reduced. For the macrocycles with furanylene-acetylene repeat units (with alternating formal $4n$ and $4n+2$ π -electron systems) discussed in the section on Type I-CA, the observed pronounced differences in the emission properties depending on the ring size may be explained by the emergence of Baird aromaticity in the macrocycles with a formal $4n$ π -electron system.⁴⁴

Molecules with Type II-CA are of interest for various applications, such as singlet fission,⁵⁵ self-healing fluorophores,⁶² photoresponsive liquid crystals,^{63,64} and molecular probes.^{60,65}

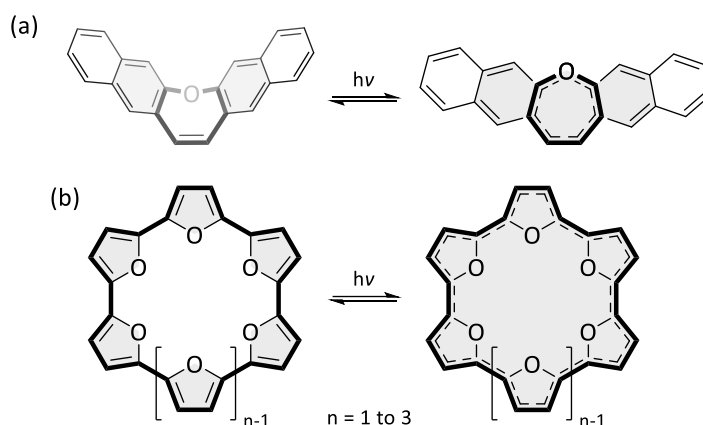


Figure 4. Examples of concealed antiaromaticity revealable upon excitation (Type II-CA): (a) dinaphthooxepine and (b) furanylene-based macrocycles planarize and become Baird aromatic upon excitation.

Concealed antiaromaticity revealable in intermolecular interactions (Type III-CA): Molecules with Type III-CA conceal their antiaromaticity as an individual molecule (in solution) but behave like antiaromatic molecules in the solid state, where energetically favourable intermolecular interactions of the $4n$ π -electron systems can occur. Such interactions can lead to intermolecular π -electron delocalization and stacked-ring aromaticity,^{7,66-68} highly interesting features for organic electronic materials. However, unfortunately, Type III-CA is the most difficult type of concealed antiaromaticity to achieve, as the antiaromaticity should only be weakly concealed for the molecules to behave like

antiaromatic compounds in intermolecular interactions. Consequently, the number of aromatic subunits in relation to the number of π -electrons in the $4n$ π -electron system should be low and the subunits should not be strongly aromatic. Furthermore, full planarity of the $4n$ π -electron system in the solid state is important for Type III-CA, as this enables the close, energetically favourable intermolecular interactions of the π -electron systems.

There are few experimental studies of stacked-ring aromaticity, but Ni(II) norcorrole derivatives were shown experimentally (and computationally) to feature stacked-ring aromaticity.⁶⁶⁻⁶⁸ In these studies, the norcorroles were covalently linked (Figure 5a) or forced to stack as dimers in micellar capsules. The interactions in these systems may be compared to the interactions in double pancake-bonded dimers, where both SOMOs of the molecules interact with the SOMOs of the same neighbouring molecule.⁶⁹ Besides these dimer interactions, also other types of highly interesting solid-state behaviour has been reported for Ni(II) norcorrole derivatives, such as chain-like stacking (Figure 5b, CCDC number: 2020183),⁷⁰ which resembles the staggered, chain-like stacking of organic biradicals that maximize SOMO-SOMO interactions by this type of stacking,^{71,72} triple-decker stacking,⁷³ and one-dimensional supramolecular assembly.⁷⁴ However, Ni(II) norcorrole derivatives cannot conceal their antiaromaticity by conformational changes in solution, due to structural restrictions. The two locally aromatic subunits can conceal the antiaromaticity to some extent, but stability issues remain, making the synthesis, purification, and processing of these compounds difficult. To increase the stability, bulky substituents can be attached to the Ni(II) norcorrole core,⁴⁰ as discussed in the section on Type I-CA above, but attaching such substituents hinders the close intermolecular interaction required for Type III-CA.

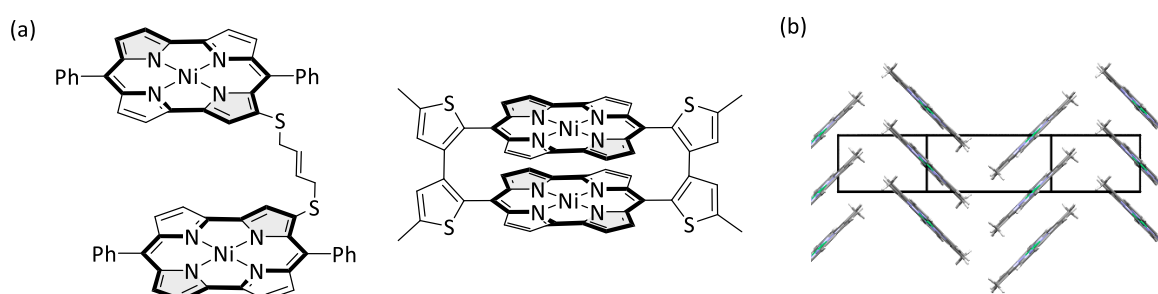


Figure 5. (a) Covalently linked Ni(II) norcorroles shown to feature stacked-ring aromaticity. (b) Chain-like stacking of methyl-substituted Ni(II) norcorroles.

As an alternative to attaching bulky substituents, designing molecules with a formal $4n$ π -electron system that are fully planar in the solid state but – in contrast to norcorroles – are capable of conformational changes to further conceal the antiaromaticity (in addition to integrating fragments of the $4n$ π -electron systems into locally aromatic subunits) may yield more stable molecules with Type III-CA. In solution, such molecules are expected to avoid coplanarity of the conformationally flexible aromatic subunits to conceal the antiaromaticity. In the solid state, however, full planarization of the molecules is expected give rise to the energetically favourable intermolecular interactions that are characteristic for $4n$ π -electron systems, potentially giving rise to stacked-ring aromaticity.

Although such a molecular design has not been investigated intentionally to date, a search of the CCDC crystal structure database afforded some structures that confirm that stable molecules with Type III-CA can be obtained by this design. The first molecule, [24]annulene tetroxide in

cis,trans,cis,trans configuration, reported by Märkl et al. in 1994,⁷⁵ is virtually planar in the solid state (Figure 6a, CCDC number: 1235045), indicating that this macrocycle revealed its antiaromaticity for energetically favourable intermolecular interactions. The macrocycle (Figure 6c) is a configurational isomer of the all-*cis* macrocycle obtained when replacing the phenylene subunits of paracyclophanetetraene (Figure 2b top) with furanylene subunits. The replacement reduces the steric demand of the subunits, allowing for the planarization in the solid state that is needed for Type III-CA. In solution, however, the [24]annulene tetroxide was reported to be highly flexible, enabling it to avoid planarity and to conceal its antiaromaticity to a large extent, as can be seen from the ¹H NMR spectra of the macrocycle at different temperatures. This is further supported by the reported stability of the macrocycle at elevated temperatures in solution. Removing the solvent, the macrocycle was obtained as stable black-violet crystals with a melting point >300 °C, indicating strong intermolecular interactions. This was confirmed by the crystal structure, which showed that each macrocycle interacts with two neighbouring macrocycles in a face-to-face fashion (Figure 6b), resembling the staggered, chain-like stacking of methyl-substituted norcorroles (Figure 5b). Besides Type III-CA, oxidation to the corresponding dication with bromine revealed that the compound also features Type I-CA. ¹H NMR measurements of the dication showed a downfield shift for the external vinylene protons and a drastic upfield shift for the two internal vinylene protons, indicating the global aromaticity of the doubly oxidized molecule. According to the authors, the “highly dynamic 24 π electron system of [the macrocycle] apparently loses its flexibility when it is oxidized”.

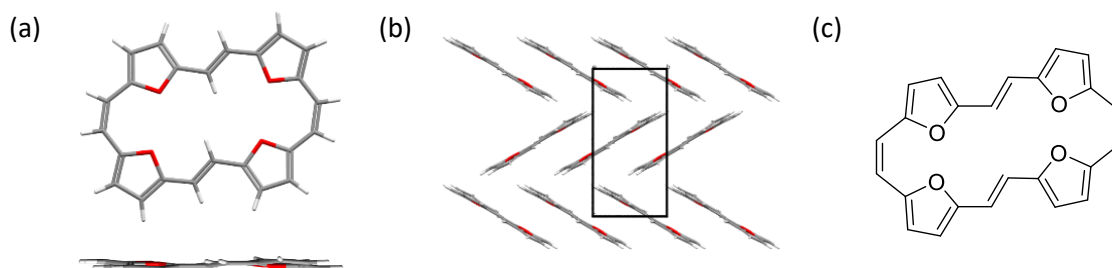


Figure 6. (a) Crystal structure, (b) packing, and (c) molecular structure of [24]annulene tetroxide in *cis,trans,cis,trans* configuration.

In contrast to [24]annulene tetroxide, the second molecule identified in the CCDC database, 5,6,17,18-bisdehydrotetrathia[24]annulene (Figure 7c, R = H), reported by Oda et al. in 1995,⁷⁶ crystallizes in dimers with face-to-face interactions (Figure 7b, CCDC number: 1314078), which resembles the Ni(II) norcorrole dimers. The obtained dark red needles of the compound showed a melting point of 242 °C. To the surprise of the authors reporting the structure, the macrocycle “has a planar X-ray structure with bent triple bonds and short S–S contacts” (Figure 7a) but “does not show antiaromatic (paratropic) properties” in solution. The ¹H NMR chemical shifts “indicate almost no conjugation around the 24 π periphery”, confirming that the antiaromaticity is effectively concealed in solution.

Interestingly, the crystal structure of the corresponding macrocycle with eight sterically demanding *n*-butyl chains attached to the thienylene subunits (Figure 7c, R = *n*-butyl) has also been reported (CCDC number: 752997).⁷⁷ In this structure, the *n*-butyl chains are considered to hinder close interactions of planarized macrocycles in the solid state, resulting in a non-planar, twisted conformation (Figure 7d). This shows that macrocycles with concealed antiaromaticity that cannot

interact closely with their neighbour(s) in the planar state or prefer other interactions, such as the macrocycle with eight *n*-butyl chains, will retain a non-planar conformation in the solid state and, hence, do not feature Type III-CA. However, twofold oxidation of the macrocycle with the *n*-butyl chains indicated that the compound does feature Type I-CA.

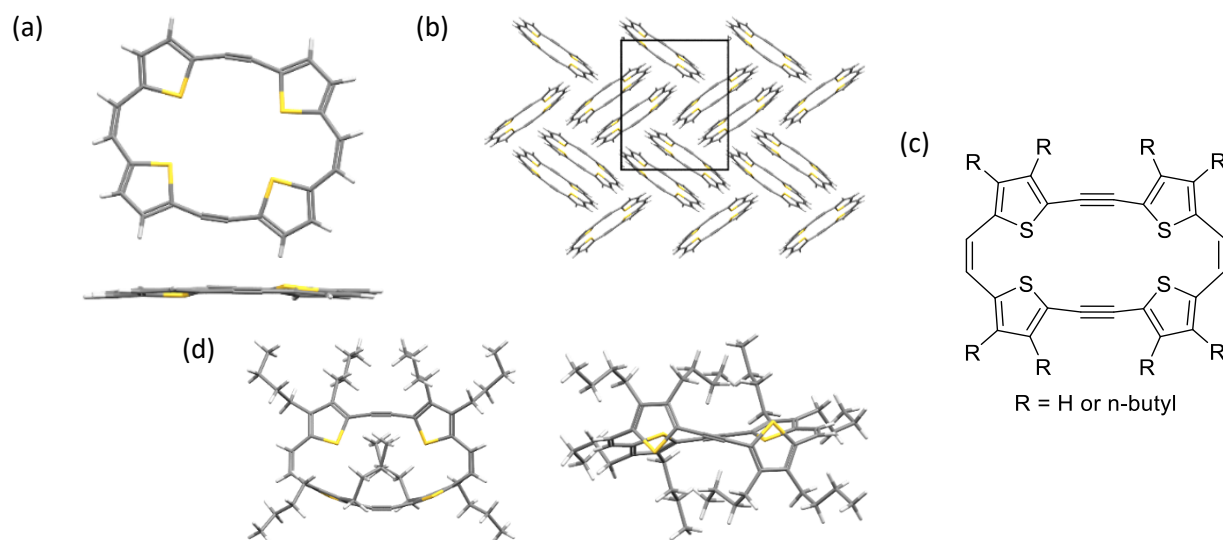


Figure 7. (a) Crystal structure and (b) packing of 5,6,17,18-bisdehydrotetrathia[24]annulene (without alkyl chains). (c) Molecular structure of the macrocycle without alkyl chains ($R = H$) and with *n*-butyl chains attached to the subunits ($R = n$ -butyl). (d) Crystal structure of the macrocycle with *n*-butyl chains.

An expanded analogue of the macrocycle with the thienylene subunits in Figure 7a was also shown to crystallize in dimers (CCDC number: 1996534),⁷⁸ whereas a contracted analogue of the macrocycle with furanylene subunits in Figure 6a exhibited chain-like packing (CCDC number: 1166262) as well as Type I-CA.⁷⁹ Other structurally related macrocycles that may feature Type III-CA can also be found in the literature, such as [24]annulene tetroxide in all-*cis* configuration and its thiophene analog.^{80,81} The ¹H NMR spectra of these compounds indicate well-concealed antiaromaticity, but their crystal structures have not been reported.

Recently, intermolecular face-to-face π - π interactions were also shown for a conformationally restricted phenylene-bridged hexaphyrin with concealed antiaromaticity (CCDC number: 2007055), despite the presence of substituents.⁸² The macrocycle crystallized in dimers and spectroscopic measurements indicated effective mutual interactions between the frontier molecular orbitals of the macrocycles in the dimers. Theoretical calculations further indicated enhanced stabilization at a close contact, suggesting the occurrence of stacked-ring aromaticity.

Type III-CA is expected to be of particular interest for supramolecular chemistry and applications in organic electronics, as the occurrence of intermolecular π -electron delocalization may benefit the intermolecular charge transport. Future investigations will help to gain a better understanding of the solid-state properties that can be achieved with Type III-CA.

In conclusion, there are numerous examples for the different types of concealed antiaromaticity (Type I to III-CA) in the literature and the corresponding effects are well described experimentally and computationally. However, until now, a term and conceptual framework to describe and

rationalize the effects and observations was missing. 'Concealed antiaromaticity' provides such a term and framework and may reconcile the different viewpoints on aromaticity and antiaromaticity of experimental chemists utilizing formal $4n$ π -electron systems in their molecular design and those who believe that the term antiaromaticity should be reserved for truly antiaromatic molecules. The concept accepts that many of the compounds claimed to be antiaromatic due to the presence of a formal $4n$ π -electron system are not truly antiaromatic. However, it acknowledges that, besides truly antiaromatic molecules, there are molecules in which the antiaromaticity is concealed to different degrees. Molecules with strongly concealed antiaromaticity can behave like antiaromatic molecules in redox reaction (Type I-CA) or upon excitation (Type II-CA) but may not behave like antiaromatic molecules in intermolecular interactions (Type III-CA), whereas molecules with weakly concealed antiaromaticity can behave like antiaromatic molecules under all these conditions.

The concept of concealed antiaromaticity will enable the conscious, rational design of molecules that show the desirable properties of antiaromatic molecules under different conditions while avoiding or diminishing the undesirable properties, namely the low stability of truly antiaromatic molecules. The increased stability is particularly useful during the synthesis, purification, and processing of the molecules, when the molecules are in solution, and will enable the development of stable functional materials with highly interesting properties that are normally ascribed to antiaromatic molecules. A broad range of applications of such materials is envisioned (and some have been reported already), ranging from organic electronics to supramolecular chemistry.

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