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OPEN LETTER

Concealed antiaromaticity

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Abstract

The literature reports numerous molecules claimed to be antiaromatic because of a formal 4*n* π-electron system. However, this neglects the actual local aromaticity of the molecules, which often feature multiple subunits with [4*n*+2] π-electrons besides the formal 4*n* 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 4*n* π-electron system but should be reserved for truly antiaromatic molecules. To reconcile the different viewpoints, the concept of concealed antiaromaticity is introduced here. Concealed antiaromaticity acknowledges that many molecules claimed to be antiaromatic are not truly antiaromatic, but they can exhibit behaviour under certain conditions that would normally be expected for antiaromatic molecules. Three types of concealed antiaromaticity are distinguished based on the conditions under which the molecules can behave like antiaromatic molecules: concealed antiaromaticity revealable in redox reactions (Type I-CA), upon photoexcitation (Type II-CA), and in intermolecular interactions (Type III-CA). The concept of concealed antiaromaticity will enable the rational design of molecules that show the desirable properties of antiaromatic molecules under the different conditions, with applications from organic electronics to photoresponsive materials, while avoiding the low stability of truly antiaromatic molecules.

Keywords

molecular design, conjugated compounds, small molecules, macrocycles, aromaticity, antiaromaticity, concealed antiaromaticity, excited-state aromaticity, stacked-ring aromaticity, redox reactions, photoexictation, intermolecular interactions

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Monocyclic molecules with a delocalized π-electron system of [4*n*+2] π-electrons, where *n* is a non-negative integer, are aromatic according to Hückel's rule, whereas with 4*n* π-electrons they are antiaromatic[1–4]. These rules of ground-state aromaticity are reversed in the lowest ππ* singlet and triplet excited states, where molecules with a cyclic delocalized system of 4*n* π-electrons are expected to be aromatic and with [4*n*+2] π-electrons to be antiaromatic according to what is known as Baird's rule[5–10]. 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 in aromatic molecules provides for enhanced thermodynamic stability compared to their acyclic structural analogues, antiaromatic molecules are less stable than their acyclic structural analogues[11]. 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 normally 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[12], 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)[13], whereas cyclobutadiene is known to dimerize (Figure 1b)[14].

Besides monocyclic 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 4*n* π-electron system but reduced diradical character (between 0 and 1)[15]. 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[16–24], even when the diradical character is low. In contrast to truly antiaromatic molecules, which may only be isolated under cryogenic conditions, these polycyclic molecules are more stable[12], with dibenzopentalene and biphenylene being readily isolable. However, the classification of such molecules as antiaromatic has been criticized, particularly for polycyclic molecules that feature both formal 4*n* and [4*n*+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 4*n* 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 4*n* π-electron system that fulfil not only the magnetic criterion but also the structural, energetic, and electronic criteria of (anti)aromaticity[25–28]. While the latter view follows a rather strict holistic approach and is in better agreement with the definition of (anti)aromaticity[11], 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. In an approach that generalized Hückel's rule to polycyclic molecules, such molecules were previously classified as intermediate, showing partially aromatic character[29], but this classification does not provide information about the properties and behaviour of the molecules. Other terms that have been suggested in informal discussions, including attenuated antiaromaticity, pseudo-antiaromaticity, or concealed 4*n* π-electron cycles, are limited in scope and not suitable for the development of a more general framework.

To reconcile the different viewpoints and to enable a rational design of molecules with the observed behaviour, the concept of 'concealed antiaromaticity' is introduced here, which provides a more general framework for understanding and explaining the properties that arise from certain structural motifs. The concept accepts that many of the molecules claimed to be antiaromatic due to the presence of a formal 4*n* 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

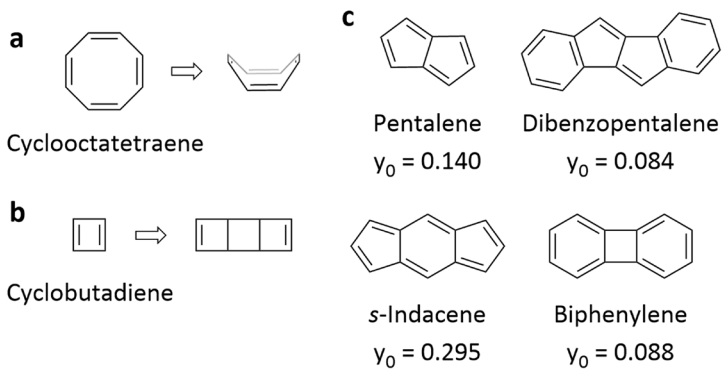

Figure 1. Antiaromaticity escape and diradical character. a,**b**, Cyclooctatetraene adopting a non-planar conformation (**a**) and cyclobutadiene undergoing dimerization (**b**) to escape antiaromaticity. **c**, Molecular structure and diradical character y_0 of pentalene, dibenzopentalene, *s*-indacene, and biphenylene. The diradical character values are from reference 15.

normally be expected for antiaromatic molecules. Quite the contrary, molecules with concealed antiaromaticity allow the desirable properties of antiaromatic molecules under the different conditions to be used without having to deal with their undesirable properties, namely the low stability of truly antiaromatic molecules.

Structural motifs of concealed antiaromaticity

Molecules with concealed antiaromaticity feature a formal 4*n* π-electron system (Figure 2, bold bonds), but additional structural units and/or conformational changes prevent this 4*n* π-electron system from turning the molecules antiaromatic. In other words, the additional structural units and the conformational changes conceal the antiaromaticity, sometimes even resulting in molecules that may also be described as locally aromatic or nonaromatic. Based on molecules described in the literature, three common structural motifs to conceal the antiaromaticity can be identified:

1. **Locally aromatic units sharing 2 π-electrons with the 4*n* 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 to large molecular propellers (Figure 2a)[21,30,31]. Formulated as a molecular design strategy starting from 4*n* annulenes, this can be described as *ortho*-fusing aromatic units with the 4*n* π-electron system.

2. **Locally aromatic units sharing 4 π-electrons with the 4*n* π-electron system**: Conjugated macrocycles often conceal their antiaromaticity in this way, including paracyclophanetetraene and cycloparaphenylenes (Figure 2b)[32–34]. Formulated as a molecular design strategy, this can be described as creating locally aromatic units along the 4*n* π-electron system by introducing 2π-electron bridges.

In both cases, fragments of the 4*n* π-electron system are integrated into locally aromatic subunits with [4*n*+2] π-electrons (Figure 2, grey shadings), but the integration of 4 π-electrons is considered to have a more pronounced effect on the antiaromaticity than the integration of 2 π-electrons. Both structural motifs can also be present in the same molecule[35,36]. Aromatic units may also be fused with more than one 4*n* π-electron system[37]. In addition to these units, the molecules are often able to further conceal the antiaromaticity by conformational changes, unless structural restrictions prevent the formal 4*n* π-electron system from adopting a non-planar conformation.

3. **Internal connections of the 4*n* π-electron system**: Covalent bonds that connect atoms of the 4*n* π-electron system directly, so without an additional structural unit, can conceal the antiaromaticity / reduce the diradical character[15]. This is particularly effective if it creates locally aromatic units (in which all π-electrons of these locally aromatic units also form part of the formal 4*n* π-electron system), as in biphenylene (Figure 2c left). However, internal connections can considerably reduce the ability of the molecules to further conceal the antiaromaticity by conformational changes. Therefore, this structural motif is often found in combination with other structural motifs (especially when the internal connection does not create locally aromatic units), as in dibenzopentalene (Figure 2c right). As a molecular design strategy, connecting the 4*n* π-electron system internally offers less flexibility, as no additional atoms are introduced.

Substituents at the 4*n* π-electron system or heteroatoms in the 4*n* π-electron system can also have an impact on the level of concealment but are normally only found in combination with one or more of the structural motifs outlined above. For example, Ni(II) norcorrole features two nitrogen atoms in the formal

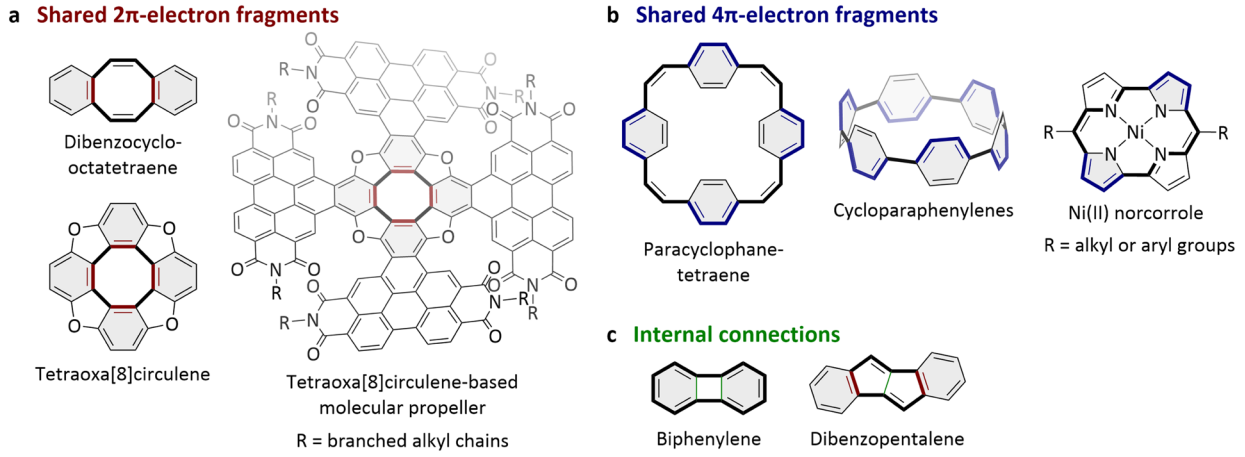

Figure 2. Structural motifs of concealed antiaromaticity. a–c, Molecules with concealed antiaromaticity, featuring a formal 4*n* π-electron system (bold bonds) as well as different structural motifs that conceal the antiaromaticity: Locally aromatic subunits (grey shadings) sharing 2 π-electrons (red; **a**) or 4 π-electrons (blue; **b**) with the formal 4*n* π-electron system or internal connections of the formal 4*n* π-electron system (green; **c**).

4*n* π-electron system, two locally aromatic subunits that share 4 π-electrons with the formal 4*n* π-electron system, as well as two vinylene substituents that bridge the π-electron system but do not create locally aromatic units (Figure 2b right). The substitution of carbon atoms in the 4*n* π-electron system with nitrogen atoms, as in Ni(II) norcorroles and as studied computationally for pentalene[38], is considered to add to the level of concealment. Other structural modifications such as the coordination to a metal atom or ion, as in cyclobutadiene–metal complexes or in Ni(II) norcorroles, may also conceal the antiaromaticity or contribute to the concealment.

Three types of concealed antiaromaticity

Concealing the antiaromaticity increases the stability of the molecules during synthesis, purification, and processing while retaining desirable properties of antiaromatic molecules (e.g. excellent stability in the doubly charged states), but which properties are retained depends on how strongly the antiaromaticity is concealed. The integration of fragments of the 4*n* 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 4*n* 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 4*n* π-electron system, and (iii) the ability or disability of the 4*n* 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 centre), which feature a high number of strongly aromatic subunits in relation to the number of π-electrons in the formal 4*n* π-electron system, or very weakly concealed like in Ni(II) norcorroles (Figure 2b right), 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 diradical character y_0 of 0.127[39], similar to the diradical character of pentalene. If the antiaromaticity is strongly concealed, the molecules may also be seen as locally aromatic (or nonaromatic in cases like cyclooctatetraene), but also for these molecules the term concealed antiaromaticity can provide useful guidance to understand the experimental properties, as these molecules can still behave like antiaromatic molecules under certain conditions. 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:

1. **Type I-CA**: Concealed antiaromaticity revealable in redox reactions
2. **Type II-CA**: Concealed antiaromaticity revealable upon photoexcitation
3. **Type III-CA**: Concealed antiaromaticity revealable in intermolecular interactions

The different types of concealed antiaromaticity are not mutually exclusive. Molecules with Type I-CA 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 identified in the literature (see also Figure 3).

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 when reduced or oxidized to the doubly charged states, where – just like truly antiaromatic molecules – the molecules become globally aromatic. This is because the formal 4*n* π-electron system transitions to a [4*n*+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, as other structural changes that result in enhanced π-electron delocalization and reduced bond-length alternation can still be possible.

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.

As structurally simple examples, both cyclooctatetraene and dibenzocyclooctatetraene planarize and become aromatic upon twofold reduction (Figure 3a)[30,40,41]. Similarly, dibenzopentalene (Figure 2c) and its derivatives were shown to become globally aromatic upon reduction to the dianion or oxidation to the dication[42,43]. Tetraoxa[8]circulene and the large molecular propeller based on this structure (Figure 2a) also switch to a globally aromatic state upon reduction[21]. Similarly, a double aza[7]helicene with a central 8 π-electron unit was shown to become aromatic upon twofold oxidation[44]. Moving on to larger formal 4*n* π-electron systems, paracyclophanetetraene (Figure 3a) and its derivatives were shown to become globally aromatic upon two-electron reduction or oxidation[45–51], although they cannot fully planarize for steric reasons. For paracyclophanetetraene, switching between a locally aromatic neutral state (with strongly concealed antiaromaticity) and a globally aromatic charged state was introduced as a platform for obtaining organic battery electrode materials[32]; even when integrated into conjugated polymer backbones, this macrocycle retains its ability to become globally aromatic upon reduction[52]. Ni(II) norcorrole (Figure 2c) also transitions to a globally aromatic state upon twofold reduction or oxidation, and the effect was used to obtain a bipolar battery electrode material[53].

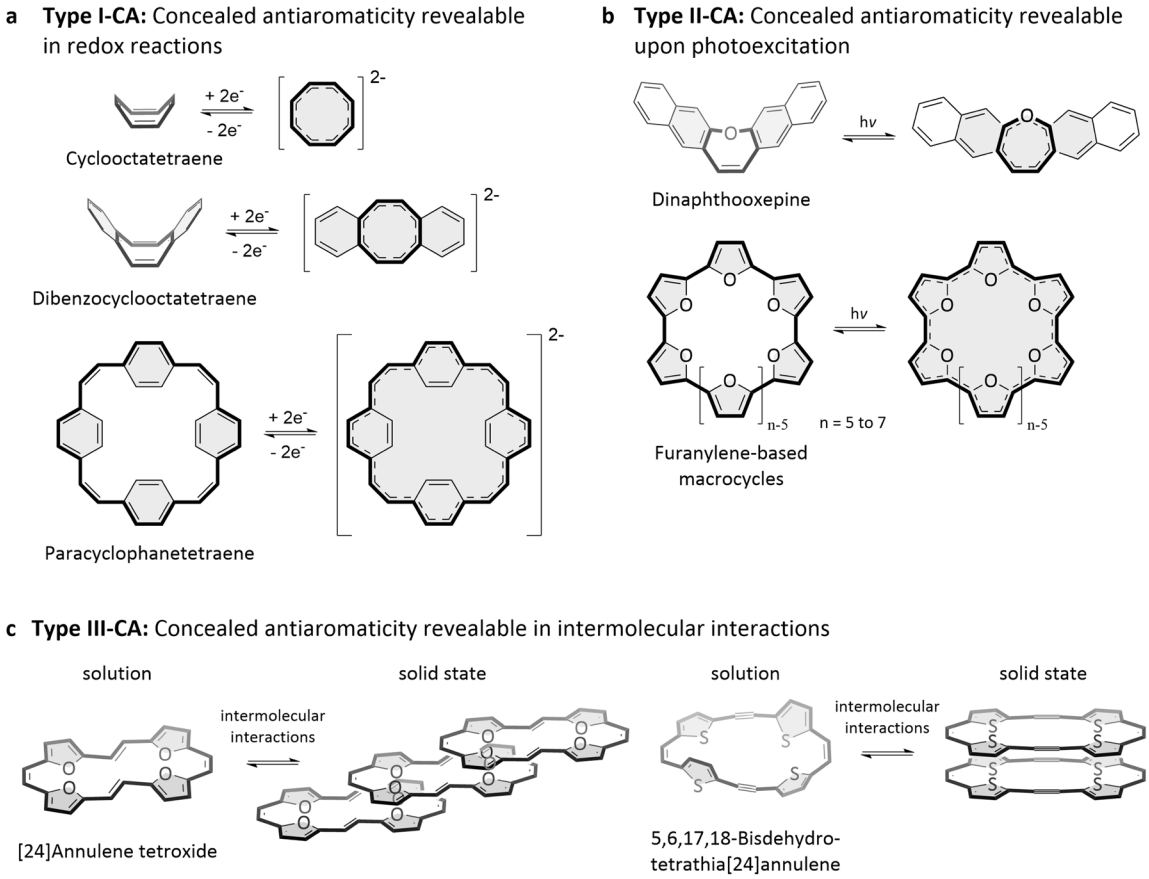

Figure 3. Three types of concealed antiaromaticity. a–**c**, Examples of molecules with concealed antiaromaticity revealable in redox reactions (Type I-CA; **a**), upon photoexcitation (Type II-CA; **b**), and in intermolecular interactions (Type III-CA; **c**). **Type I-CA**: Cyclooctatetraene and dibenzocyclooctatetraene planarize and become aromatic upon twofold reduction. Paracyclophanetetraene cannot fully planarize but can still become globally aromatic in redox reactions. **Type II-CA**: Dinaphthooxepine and furanylene-based macrocycles planarize and become Baird aromatic upon photoexcitation. **Type III-CA**: [24]Annulene tetroxide and 5,6,17,18-bisdehydrotetrathia[24]annulene planarize and show chain-like/dimer stacking in the solid state.

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. Larger macrocycles, such as cycloparaphenylenes (Figure 2b) of different size, can also reveal their concealed antiaromaticity in redox reactions[33,34,54–56]. In these macrocycles, each phenylene subunit contributes 4 π-electrons to the formal macrocyclic 4*n* π-electron system, meaning that all cycloparaphenylenes that were studied featured Type I-CA (independent of the number of subunits). In contrast, each of the repeat units of furanylene-acetylene macrocycles contributes 6 π-electrons to the formal macrocyclic π-electron system, resulting in alternation between formal 4*n* and [4*n*+2] π-electron systems with increasing ring size[57]. Those with a formal 4*n* π-electron system were more readily oxidized in cyclic voltammetry measurements, indicating Type I-CA. For the neutral macrocycles, the authors compared the properties to those of the corresponding phenylene-acetylene macrocycles, which showed that the antiaromaticity is more strongly concealed with phenylene than with the furanylene subunits. Other examples of macrocycles with Type I-CA include oligofuran and alternating furan-thiophene macrocycles[58–60], expanded carbaisophlorinoids[61], heteroatom-substituted porphyrinoids of different size[62], and porphyrin-based nanorings[63,64].

Concealed antiaromaticity revealable upon photoexcitation (Type II-CA): Molecules with Type II-CA conceal their antiaromaticity in the ground state but behave like antiaromatic molecules when photoexcited to 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 photoexcitation 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 (Figure 1) and their derivatives[65–70]. Studies on π-expanded oxepines (Figure 3b) and other 8π-electron heterocycles with

locally aromatic units fused with the formal 8π-electron system show that these molecules can also feature Type II-CA[71–75]. Moving on to conjugated macrocycles, paracyclophanetetraene (Figure 3a) and its derivatives also feature Type II-CA according to computations and experimental indications[47–50]. The results of computational studies of cycloparaphenylenes (Figure 2b) of different size and their furanylene analogues (Figure 3b) show that – with both types of subunits – these macrocycles can feature Type II-CA[76]. 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. 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 pronounced differences in the emission properties depending on the ring size indicate Type II-CA for those macrocycles with a formal $4n$ π-electron system[57]. In a host-guest complex of a fullerene and a macrocycle composed of benzene-fused pyrrolo[3,2-b]pyrrole units with Type II-CA[77], Baird aromaticity may play a role in rendering the locally excited state at the macrocycle the lowest excited state of the complex. The photoresponsive behaviour of a borole fused with aromatic units may also be explained by Type II-CA[78].

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. These interactions can lead to intermolecular π-electron delocalization and stacked-ring aromaticity[12,79–81], which are highly interesting features for organic electronic materials. In contrast to truly antiaromatic molecules, no covalent bonds between the molecules are formed as a result of the interactions. Unfortunately, however, 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 molecules in intermolecular interactions, meaning that the number of aromatic subunits in relation to the number of π-electrons in the $4n$ π-electron system should be low and no strongly aromatic subunits should be present. This requirement needs to be carefully balanced with the stability requirements. 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.

Ni(II) norcorrole derivatives (Figure 2b) can fulfil these requirements and, indeed, were shown to feature stacked-ring aromaticity when stacked as dimers in micellar capsules or connected via linkers[79–81]. The molecular orbital interactions in these systems may be compared to the SOMO-SOMO interactions in double pancake-bonded dimers[82]. Besides these dimer interactions, also other types of highly interesting solid-state behaviour has been reported for norcorrole derivatives, such as chain-like stacking[83], which resembles the staggered, chain-like stacking of organic biradicals that maximize SOMO-SOMO interactions by this type of stacking[84,85], triple-decker stacking[86], and one-dimensional supramolecular assembly[87]. However, as discussed above, bulky substituents can be required to sufficiently increase the stability of Ni(II) norcorrole derivatives for applications, but these hinder the close intermolecular interaction required for Type III-CA.

As an alternative to attaching bulky substituents, designing molecules with a formal $4n$ π-electron system that fulfil the above requirements but – in contrast to Ni(II) 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 to give rise to the energetically favourable intermolecular interactions that are characteristic for $4n$ π-electron systems, potentially giving rise to stacked-ring aromaticity. Stable molecules with Type III-CA following this molecular design have been observed in the literature; the first macrocycle, [24]annulene tetroxide in *cis*,*trans*,*cis*,*trans* configuration (Figure 3c), was reported to be virtually planar in the solid state (Figure 4a)[88], indicating that it revealed its antiaromaticity for energetically favourable intermolecular interactions. The macrocycle is a configurational isomer of the all-*cis* macrocycle obtained when replacing the phenylene subunits of paracyclophanetetraene (Figure 3a) with furanylene subunits. The furanylene subunits are less aromatic and less sterically demanding than phenylene subunits, which reduces the degree of concealment and allows for planarization in the solid state. In solution, however, [24]annulene tetroxide was reported to be highly flexible, enabling it to avoid planarity and to conceal its antiaromaticity to a large extent. The black-violet crystals of the macrocycle showed a melting point >300 °C and a staggered, chain-like face-to-face stacking (Figure 4a bottom), resembling the stacking of methyl-substituted Ni(II) norcorrole[83]. Besides Type III-CA, [24]annulene tetroxide also features Type I-CA according to ^{1}H NMR measurements of its dication. It was reported that the "highly dynamic 24 π electron system of [the macrocycle] apparently loses its flexibility when it is oxidized".

In contrast to [24]annulene tetroxide, 5,6,17,18-bisdehydrotetrathia[24]annulene (Figure 3c), another macrocycle that follows the proposed molecular design, was reported to crystallize in dimers with face-to-face interactions (Figure 4b)[89], resembling the Ni(II) norcorrole dimers. The 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" but "does not show antiaromatic (paratropic) properties" in solution, 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 has also been reported (Figure 4c)[90]. Here, the *n*-butyl chains are considered to hinder close interactions of the $4n$ π-electron systems in the solid state, resulting in a non-planar,

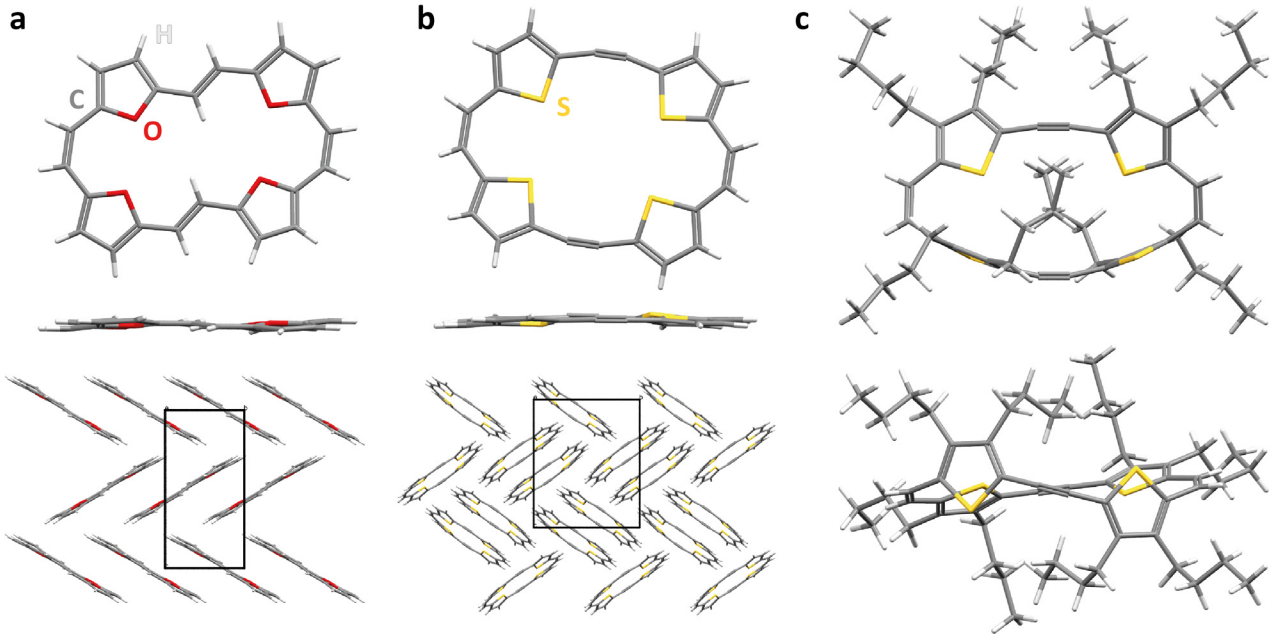

Figure 4. Crystal structures and packing of annulenes with concealed antiaromaticity. a,b, Crystal structure and packing of [24]annulene tetroxide in *cis,trans,cis,trans* configuration (**a**) and 5,6,17,18-bisdehydrotetrathia[24]annulene (**b**). The corresponding molecular structures are shown in Figure 3c. **c**, Crystal structure of 5,6,17,18-bisdehydrotetrathia[24]annulene with eight *n*-butyl chains attached to the thienylene units.

twisted conformation and in yellow crystals with a significantly lower melting point of 116 °C. This shows that macrocycles with concealed antiaromaticity that cannot interact closely with their neighbour(s) in the planar state or prefer other interactions will retain a non-planar conformation in the solid state and, hence, do not feature Type III-CA. However, oxidation of the macrocycle indicated that the compound does feature Type I-CA.

An expanded analogue of 5,6,17,18-bisdehydrotetrathia[24] annulene was also shown to crystallize in dimers[91], whereas a contracted analogue of [24]annulene tetroxide exhibited chain-like packing and Type I-CA[92]. Recently, dimer interactions were also shown for a conformationally restricted phenylene-bridged hexaphyrin with concealed antiaromaticity, despite the presence of sterically demanding substituents[93].

Practical utility of the concealed antiaromaticity conceptual framework

The concept of concealed antiaromaticity and the structural motifs and design strategies described in this article will enable the conscious, rational design of molecules that exhibit the desirable properties of antiaromatic molecules in redox reactions, upon photoexcitation, and in intermolecular interactions. Moreover, tailoring molecules and materials based on this conceptual framework can facilitate their preparation, processing, and application by avoiding or diminishing the undesirable low stability of antiaromatic compounds.

By considering the factors impacting the degree of concealment, molecules with different types of concealed antiaromaticity can be obtained, each type being ideal for different applications: (i) As shown for several molecules with Type I-CA, this type of concealed antiaromaticity is highly interesting for battery electrode materials, as the stability of the charged states is improved by the occurrence of global aromaticity, addressing a common issue of currently used organic battery electrode materials. At the same time, concealing the antiaromaticity in the neutral state ensures that the stability of the neutral state is not affected, enabling excellent reversibility of the redox reaction. It is envisioned that Type I-CA can also be an interesting feature for other applications that involve redox reactions, such as electrocatalysis and photoredox catalysis, where it may facilitate charge accumulation. For molecules with Type I-CA that undergo planarization upon reduction or oxidation, applications that can exploit this reversible conformational change are also promising. (ii) Similarly, molecules with Type II-CA are of interest for various applications, including singlet fission[69], as self-healing fluorophores[94], photoresponsive liquid crystals[95,96], and molecular probes[74,97]. Applications in singlet fission exploit the low energy of the lowest triplet excited state relative to the energy of the lowest singlet excited state of molecules with Type II-CA, a property related to the Baird aromaticity. The relative energies of the two states can be tuned depending on the degree of concealment. Self-healing fluorophores can be obtained by covalently linking a fluorophore to a molecule with Type II-CA, which can act as a quencher

of the otherwise long-lived, nonfluorescent triplet state that occurs if the fluorophore undergoes intersystem crossing. The process benefits from the Baird aromaticity of molecules with Type II-CA in the lowest triplet excited state, improving the performance of the fluorophore and avoiding the formation of reactive oxygen species. Photoresponsive liquid crystals and molecular probes both exploit the planarization of molecules with Type II-CA upon photoexcitation, requiring them to be conformationally flexible. (iii) Type III-CA is expected to be of particular interest for organic electronics and supramolecular architectures. Both applications utilize the close, energetically favourable intermolecular interactions of the π-electron systems of molecules with Type III-CA. In organic electronics, the effective intermolecular π-electron delocalization that can arise from these interactions is expected to enable materials with excellent intermolecular charge transport properties, potentially benefiting from stacked-ring aromaticity. In supramolecular chemistry, the energetically favourable intermolecular interactions can act as a driving force for self-assembly.

Conclusion

The concept of concealed antiaromaticity helps resolve the argument about the terminology to be used for a class of molecules that feature both formal $4n$ and $[4n+2]$ π-electron systems, without requiring a change of the definition of aromaticity and antiaromaticity. Not introducing a new type of (anti)aromaticity, the term describes that a molecule behaves like an antiaromatic molecule under certain conditions rather than describing the (anti)aromaticity of its neutral ground state. Thereby, the term is not limited to antiaromatic molecules but can also be suitable for locally aromatic or nonaromatic molecules if they show the described behaviour. They can be classified as molecules with strongly concealed antiaromaticity, as opposed to molecules with weakly concealed antiaromaticity. In order to avoid any confusion, it is recommended to use the phrase "molecules with concealed antiaromaticity" rather than "concealed antiaromatic molecules".

In contrast to other terms that have been proposed, concealed antiaromaticity provides a more general framework for understanding and explaining the properties that arise from certain structural motifs, with a potential of being expanded to 'concealed aromaticity'. It can also serve as a blueprint for others to develop and explore further, better molecules and materials for various research areas and applications.

Ethics and consent

Ethical approval and consent were not required.

Data availability

No data are associated with this article.

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In this article the author proposes the introduction of “concealed antiaromaticity” as a terminology to describe the nature of molecules that could be antiaromatic regarding their 4n p-electron count contained within a closed loop but they are rather weakly antiaromatic or even non-aromatic, as their antiaromaticity is in some way diminished, however, under certain conditions they still do show characteristics typical of antiaromatic compounds. In my view this proposal is very appropriate and timely. It is a good approach to reconcile different, seemingly opposing viewpoints. Similar terms have been used before; however, they all seem to be less general or have a slightly different meaning than the concept introduced here. Notably, they have not been as clearly formulated as has been done in the present article. It is important to stress that it does not claim to be a proposal for a new definition of antiaromaticity, it merely represents a new terminology for molecules showing the properties mentioned. It should account for many compounds that may have been disregarded for a certain use where antiaromatic character could be exploited because they have been assessed weakly antiaromatic or non-aromatic, although diminishing – or concealing – their antiaromatic character may be particularly beneficial for the specific application. Indeed, we have just reported on a novel boraporphyrinoid to which the terminology proposed herein applies particularly well (refer to 1), and we have already taken it up for the description thereof. I generally support the concept proposed, and I believe that it will also be adopted by other researchers for the description of their own results – it may possibly even stimulate the design of new materials for specific applications.

There are still some issues that I would like to point out. The following suggestions could help to further improve the present manuscript and/or to avoid misunderstandings:
1) As mentioned before, there is a certain risk of misunderstanding of the proposed terminology as a new type or definition of antiaromaticity. This point is very clearly formulated in the Conclusion section. It would be advisable to formulate it in a similarly clear way early in the paper – perhaps at the end of the introduction.
2) The other related concepts mentioned such as “antiaromaticity relief” should be cited and briefly discussed in the paper. The following is stated in this regard in the introduction: “Other terms that have been suggested in informal discussions, including attenuated antiaromaticity,

pseudo-antiaromaticity, or concealed 4n p-electron cycles, are limited in scope and not suitable for the development of a more general framework." It would be useful if the author could briefly explain what these terms have been proposed for and why they are considered unsuitable. Furthermore, there is no citation given. Have these terms never been defined in a written form? In that case, would it be useful to mention them here? Perhaps they should then be put in a footnote.
3) The article contains four figures that each have three parts numbered as **a**, **b**, and **c**. If one skims quickly over the article, one could get the impression that there is an interconnection between them, especially between the three different structural motifs of concealed antiaromaticity and the three types of concealed antiaromaticity. I discussed this with a colleague who confirmed my view. For example, one could erroneously assume that it is claimed that molecules with the structural motif **a** conceal their antiaromaticity according to Type I-CA. Of course, it becomes clear that this is not the case when you read the article. However, this potential misinterpretation for the less careful reader can be avoided by using different types of numbering. Furthermore, in the text a different numbering, 1, 2, 3, is used rather than **a**, **b**, **c**. Actually, in the case of Figure 3, further numbering could be omitted, as the three types are already denoted as "Type I-CA" etc., so **a**, **b**, **c** and 1, 2, 3 are superfluous.
4) There are some issues regarding the compilation of different types of structural motifs of concealed antiaromaticity presented in Figure 2. I agree that it is useful to make such a distinction; however, the classification provided is not comprehensive. For example, as mentioned before, heteroatoms are not considered. In our above-mentioned example, shared 4p-electron fragments are present, and the antiaromaticity is concealed by bridging sulfur atoms. Heteroaromaticity or sigma-aromaticity and other more "exotic" forms are not included into the classification provided. Furthermore, should a deviation from planarity also be regarded as a way to conceal antiaromaticity? I think it is not necessarily needed to provide a comprehensive classification, but it should be clearly stated that this is not the case. I suggest writing that the classifications cover "the most common motifs in organic chemistry" (or a similar formulation).
Although I find it useful to include "internal connections" as a third classification in the figure, there are certainly ambiguities. For instance, biphenylene can be regarded as a twofold-internally connected [12]annulene or as a twofold-benzannulated cyclobutadiene (type **a**), respectively. There are several other possibilities for the second example as well. These ambiguities should be mentioned.
5) A bit problematic is the point that it is often referred to different degrees of antiaromaticity concealment, but there is no criterion for quantification provided. Could perhaps the diradical character y_0 be utilized as suggested before?
Page 4, top right: "… but the integration of 4 p-electrons is considered to have a more pronounced effect on the antiaromaticity than the integration of 2 p-electrons." Could a reference be given for this claim or has this been noted here for the first time? Perhaps it could be explained how this conclusion has been drawn.
Page 5: "The integration of fragments of the 4*n* p-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 4*n* p-electron system, …" Could a reference be given for this claim? Can this be quantified? It has been noted that local aromaticity and global antiaromaticity may coexist in some cases.
In the last section before the Conclusion, "Practical utility of the concealed antiaromaticity conceptual framework", several examples of possible applications are provided. In the last passage of that section (page 8 bottom and page 9) there are no references given. I was wondering if some references are missing here, or have these suggested applications never been realized with this class of compounds yet? In that case, perhaps references where these

applications have been realized in general (though with other compound classes) could be cited.

References

1. Buckel M, Klopf J, Schneider JS, et al.: A fully conjugated meso-boron-substituted porphyrinoid combining Lewis acidity with redox-switchable aromaticity. Nat. Commun. 2025; 16: 1775.

Is the rationale for the Open Letter provided in sufficient detail? (Please consider whether existing challenges in the field are outlined clearly and whether the purpose of the letter is explained)

Yes

Does the article adequately reference differing views and opinions?

Partly

Are all factual statements correct, and are statements and arguments made adequately supported by citations?

Partly

Is the Open Letter written in accessible language? (Please consider whether all subject-specific terms, concepts and abbreviations are explained)

Yes

Where applicable, are recommendations and next steps explained clearly for others to follow? (Please consider whether others in the research community would be able to implement guidelines or recommendations and/or constructively engage in the debate)

Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Synthetic Inorganic / Organic Chemistry; Computational Chemistry; Macromolecular Chemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 30 May 2025

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Gokulnath Sabapathi

Indian Institute of Science Education and Research Thiruvananthapuram, Vithura, Kerala, India

Recommendation: ***Accept with Minor Revisions***

This work outlines a conceptual framework referred to as "concealed antiaromaticity," aiming to clarify discrepancies observed in the categorization of certain 4nπ-electron systems. Although these molecules are formally expected to exhibit antiaromatic behaviour based on electron-counting approaches, many deviate from this prediction. Their unexpected thermodynamic stability and the absence of typical antiaromatic features can be attributed to geometric and electronic modifications that hinder effective π-electron delocalization. The author proposes three forms of concealed antiaromaticity, each triggered by different conditions. **Type I-CA** appears during redox changes, **Type II-CA** under photoexcitation, and **Type III-CA** through intermolecular interactions.

The article presents several strengths. It introduces the concept of "concealed antiaromaticity," offering a useful framework to explain π-systems that deviate from traditional aromaticity rules. The classification into three types of CA is logically structured and helps guide both molecular design and application. The paper also provides clear design principles based on structural motifs that influence antiaromatic behaviour. Moreover, the discussion effectively highlights potential uses in redox chemistry, molecular electronics, and photoresponsive materials. However, there are certain areas where the manuscript can be improved:

1. 1. The paper does not define measurable parameters (e.g., NICS, diradical indices, HOMO–LUMO gaps) to assess the degree of antiaromaticity concealment, this can be included.
   2. The role of Baird aromaticity in **Type II-CA** is insufficiently addressed; a deeper theoretical and mechanistic discussion is expected before I arrive for a positive decision.
   3. It would be good if the authors can provide tabular summaries or comparative data to help evaluate and visualize examples more systematically.
   4. Some systems described as “concealed antiaromatic” may also fall under existing categories such as fluxional aromaticity or pseudoaromaticity. Discussing the overlap or differences with these existing terms would help the term “concealed antiaromaticity” with more distinctly within the reported examples.

Is the rationale for the Open Letter provided in sufficient detail? (Please consider whether existing challenges in the field are outlined clearly and whether the purpose of the letter is explained)

Yes

Does the article adequately reference differing views and opinions?

No

Are all factual statements correct, and are statements and arguments made adequately supported by citations?

Yes

Is the Open Letter written in accessible language? (Please consider whether all subject-specific terms, concepts and abbreviations are explained)

Partly

Where applicable, are recommendations and next steps explained clearly for others to follow? (Please consider whether others in the research community would be able to implement guidelines or recommendations and/or constructively engage in the debate)
No

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Pi conjugated planar antiaromatic and helically chiral macrocycles.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Reviewer Report 25 April 2025

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Roy Lavendomme
Université libre de Bruxelles, Brussels, Belgium

In this article the author proposes the new terminology of “concealed antiaromaticity” to classify molecules that show “weakened” antiaromaticity to no (anti)aromaticity in their neutral ground state but still behave like antiaromatic compounds under certain conditions.
This article is **not** about defining antiaromaticity or antiaromaticity criteria which is an entirely separate ordeal already undertaken by others in the literature attempting to complement the current IUPAC definitions.
Overall, I appreciate the will to expand the compendium of scientific terminology to better categorize individual studies, thus facilitating literature research and discussion within the scientific community. In particular, when developing applications that make use of antiaromatic compounds properties, non aromatic compounds may be disregarded in early stages but, as clarified in this article, some may still display desired properties like antiaromatic compounds under specific conditions. Referring to such non aromatic compounds as “compounds with concealed antiaromaticity” may place them in the spotlight along antiaromatic compounds for application development.
I am unsure if this concept of “concealed antiaromaticity” will find significant usage but it deserves to be proposed as, to the best of my knowledge, there is no equivalent existing concept (even if it partly overlaps with some terminology related to antiaromaticity).
Some points addressed in the article are still unclear to me as listed below and should be clarified. If the concept is adopted by the community, it will likely be further refined in the long run.

1. It is made clear in the conclusion that this “concealed antiaromaticity” is not meant to define a new type of (anti)aromaticity nor a criterion of antiaromaticity. I would recommend to

make such a clear disclaimer in the introduction to prevent readers from getting the wrong idea about what concept is presented therein. Indeed, reading the abstract, I first thought this concept was meant to describe weakened antiaromatic rings which then puzzled me when I saw examples of non aromatic compounds such as cyclooctatetraene.

2. The author regularly refers to different degrees of antiaromaticity concealment. Could the author clarify what the degree of concealment refers to and perhaps a criterion that could be used to categorize between weak and strong concealment? I presume (but could be wrong) that strongly concealed antiaromaticity refers to non aromatic molecules (e.g. bent cyclooctatetraene) whereas weakly concealed antiaromaticity refers to molecules containing weakly antiaromatic rings (e.g. tetraoxacirculene). In the introduction, the author presents the diradical character to define truly antiaromatic molecules but does not quantitatively refer to this criterion when addressing the degree of concealment.
3. I worry that using the word “antiaromaticity” for this concept may lead to confusion for non-experts when referring to molecules that do not meet criteria of antiaromaticity at any given point (e.g. non aromatic cyclooctatetraene). Perhaps the author could propose a solution to ensure that non experts would not wrongly assume that molecules with completely concealed antiaromaticity (i.e. non aromatic) are “antiaromatic”. I do believe that the recommendation made in the penultimate paragraph of the conclusion is insufficient. A solution could be to clearly state “non aromatic molecule with concealed antiaromaticity”, when applicable.
4. The difference between the structural motifs of concealed antiaromaticity “shared 2π-electron fragments” and “internal connections” appears to be arbitrary to me. Few examples:

- One could argue that the dibenzopentalene is a [16] annulene with 3 internal connections. Yet, it is presented in Fig 2c as being a cyclooctatetraene with 1 internal connection (= pentalene) and 2 shared 2π-electron fragments (with benzene rings).
- Biphenylene is represented in Fig 2c as a cyclododecahexaene ([12] annulene) with two internal connections but it could be considered as a cyclobutadiene with 2 shared 2π-electron fragments (with benzene rings).
- Pentalene (antiaromatic) could be viewed as a cyclooctatetraene (initially non aromatic) with 1 internal connection. This would mean that the structural motif of concealed antiaromaticity (i.e. internal connection) leads to an increase in antiaromaticity instead of decreasing it!

I think that each structural motif for antiaromaticity concealment can be categorized in the first two types: shared 2π-electron fragments and shared 4π-electron fragments (perhaps with the addition of heteroatoms as a third category). The internal connections category is not useful, and I would personally remove it.

Is the rationale for the Open Letter provided in sufficient detail? (Please consider whether existing challenges in the field are outlined clearly and whether the purpose of the letter is explained)

Yes

Does the article adequately reference differing views and opinions?

Yes

Are all factual statements correct, and are statements and arguments made adequately supported by citations?

Yes

Is the Open Letter written in accessible language? (Please consider whether all subject-specific terms, concepts and abbreviations are explained)
Yes

Where applicable, are recommendations and next steps explained clearly for others to follow? (Please consider whether others in the research community would be able to implement guidelines or recommendations and/or constructively engage in the debate)
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Organic synthesis; Supramolecular chemistry; Reticular chemistry; Computational chemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 28 March 2025

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Miquel Solà
University of Girona, Girona, Spain

In this paper, the author introduces the concept of concealed antiaromaticity. The work describes several antiaromatic systems that are stabilized in redox reactions, by photoexcitation, or by intermolecular interactions. To put my comments in context, let me first give the basis of my arguments:

1. I am not particularly in favor of introducing new forms of aromaticity except if they are strictly necessary (see Front. Chem. 5 (2017) 22).
2. I consider the best definition of aromaticity to be that provided by Chen et al. in 2005 (Chem. Rev. 105 (2005) 3842), who defined aromaticity as *"a manifestation of electron delocalization in closed circuits, either in two or in three dimensions. This results in energy lowering, often quite substantial, and a variety of unusual chemical and physical properties. These include a tendency toward bond length equalization, unusual reactivity, and characteristic spectroscopic features*." Therefore, the two primary characteristics of aromaticity are aromatic stabilization and electronic delocalization, while ring currents are secondary features.
3. Aromatic stabilization is large in small rings and becomes residual in large rings (see J. Am.

Chem. Soc. 143 (2021) 2403 & Chem. Sci., 16 (2025) 5613).

Having established the basis of my discussion, my comments are the following:

1. What is the difference between the term “concealed antiaromaticity” and “antiaromaticity relief” or “antiaromaticity alleviation” that has been used many times before the concept of “concealed antiaromaticity” was proposed (see for a few examples: Angew. Chem. Int. Ed. 60 (2021) 25082; Nat. Commun. 12 (2021) 5409; Chem. Sci. 15 (2024) 5225; J. Am. Chen. Soc. 142 (2020) 10942, etc.)? In all cases, the idea is that the antiaromaticity of a certain ring is reduced by redox reactions, photoexcitation, π-π interactions, or benzoannulation to explain the behavior of a certain compound. I do not see what the community gains by changing “antiaromaticity relief” to “concealed antiaromaticity.”
2. Let’s consider dibenzocyclooctatetraene in Figure 2a. I find the description of this molecule using the Glidewell-Lloyd rule (GLR) much more informative (see Theor. Chem. Acc., 135 (2016) 205) than the information I get from classifying it as a molecule with concealed antiaromaticity. With the GLR, I learn which is the best resonance structure to define this molecule, and, consequently, I learn which are the positions readier to react, for instance, as a dienophile in a Diels-Alder reaction. Same for tetraoxo[8]circulene. I find it much better to stay with the GLR rather than to change to the concealed antiaromaticity concept.
3. Ni(II) norcorrole is antiaromatic according to the magnetic criterion, but its stability comes from the local aromaticity of the dipyrril fragments (Sci. Rep. 9 (2019) 4852). In general, there is no tug-of-war between local aromaticity and global aromaticity as written in the manuscript. As to the aromatic stabilization energy, local aromaticity is more important than global aromaticity (see J. Am. Chem. Soc. 143 (2021) 2403 & Chem. Sci., 16 (2025) 5613), despite the magnetic criterion indicating the opposite in many situations.
4. I think it is wrong to classify paracyclophanetetraene (Figure 2b) as a molecule with concealed antiaromaticity. From the point of view of aromaticity, this molecule holds four π-sextets that provide about 120 kcal/mol of aromatic stabilization energy. The possible destabilization due to the antiaromaticity of the 24 π-electron circuit is minor (see J. Am. Chem. Soc. 143 (2021) 2403 & Chem. Sci., 16 (2025) 5613). Maybe one can classify paracyclophanetetraene as antiaromatic because of the existence of paratropic ring currents, but, if so (I do not know), then the classification is an artifact due to the use of ring currents as indicator of aromaticity. Same for cycloparaphenylenes.
5. Biphenylene is better described as an aromatic molecule with two π-sextets that become a 12π-electron Baird aromatic species in the lowest-lying triplet excited state (see J. Org. Chem., 82 (2017) 6327).
6. How can one distinguish between antiaromatic molecules and molecules with concealed antiaromaticity? All antiaromatic molecules are of types I-CA and/or II-CA and/or III-CA. If molecules with concealed antiaromaticity behave like antiaromatic molecules, then let’s call them antiaromatic.
7. I suggest the author mention that the aromaticity in π-π dimers is not related to “concealed antiaromaticity” but is caused by double-triplet [$^1(T_1T_1)$] and intermolecular charge-transfer (CT) electron configurations mixing substantially in the ground state wavefunctions of the dimer (see Chem. Sci. 16 (2025) 1707).
8. I do not see how the concept of “concealed antiaromaticity” can improve our molecular designs. For instance, molecules with singlet fission properties have been designed with the current concepts about aromaticity without the need to invoke a new concept (see ref. 69). Same for the other molecular designs described.

Is the rationale for the Open Letter provided in sufficient detail? (Please consider whether

existing challenges in the field are outlined clearly and whether the purpose of the letter is explained)
Yes

Does the article adequately reference differing views and opinions?
Partly

Are all factual statements correct, and are statements and arguments made adequately supported by citations?
No

Is the Open Letter written in accessible language? (Please consider whether all subject-specific terms, concepts and abbreviations are explained)
Yes

Where applicable, are recommendations and next steps explained clearly for others to follow? (Please consider whether others in the research community would be able to implement guidelines or recommendations and/or constructively engage in the debate)
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Theoretical and computational chemist

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.