Concealed Coronoid Hydrocarbons with Enhanced Antiaromatic Circuit Contributions as Models for Schottky Defects in Graphenes

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Abstract: Coronoids with holes shaped like an odd carbon benzenoid have antiaromatic holes and antiaromatic conjugated circuits. Another class of concealed diradical coronoids has been identified. They are Hückel molecular orbital diradicals (HOMO = LUMO = 0, each with a single electron occupancy) that have VB (valence-bond) structures ($K \neq 0$). This new class of concealed diradical coronoids have more enhanced antiaromatic contributions. The smallest holes in graphenes are spin polarized and have antiaromatic characteristics.

INTRODUCTION

The number of Kekulé resonance structures (K) and isomers of coronoid hydrocarbons have been enumerated by Cyvin, Gutman, and coworkers [1]. Coronoid hydrocarbons with holes shaped like an odd carbon benzenoid, like coronphene ($C_{36}H_{18}$) which has phenalenyl-like hole, have antiaromatic holes and antiaromatic circuit (4n conjugated circuits) contributions [2]. Graphene defects having holes that are shaped like benzenoids occur without distorting the planar layer whereas defects with holes that are shaped like other ring-size motifs result in distortion of graphene layer. In a prior paper, [2] we examined the latter type of defect. Herein, we will examine the former type of defect in model coronoid systems.

Antiaromaticity

The concept of antiaromaticity was introduced by Ronald Breslow [3]. In regard to the energy of a molecular system, antiaromaticity is a more destabilizing phenomenon than aromaticity is stabilizing. This can be seen by comparing the resonance energies per electron for benzene and cyclobutadiene, respectively, by various methods: conjugated circuit theory gives 0.140 eV/electron and $-$ 0.163 eV/electron [4], topological resonance energy (TRE) gives 0.0455 β/electron and $-$0.306 β/electron [5], and the Hess and Schaad resonance energy per electron (REPE) gives 0.092 eV (0.065 β) and $-$ 0.381 eV ($-$ 0.268 β) [6]. Higher *ab initio* calculations by von Rague Schleyer and coworkers [7] give aromatic stabilization/antiaromatic destabilization energies of 29.0 Kcal/mol (4.83 kcal/mol per carbon) for benzene and $-$ 31.4 kcal/mol ($-$ 7.85 kcal/mol per carbon) for bond alternant cyclobutadiene. Previously we have argued that in general antiaromatic molecules have 4n conjugated circuits, are HMO diradicals, but are VB nonradicals [8]. This theme is continued herein.
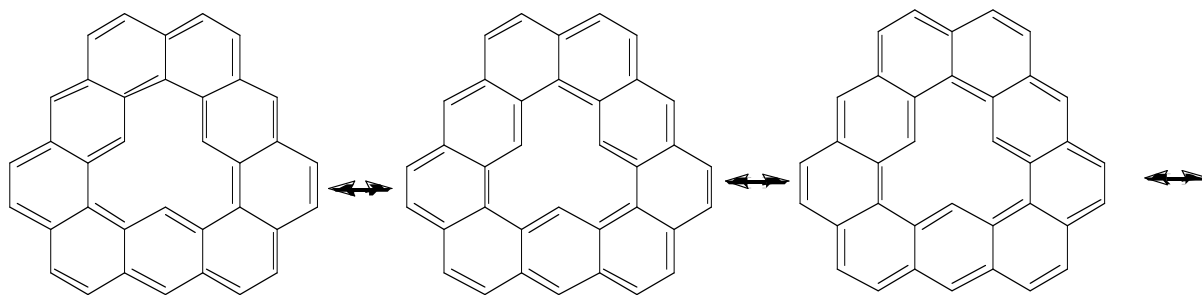
RESULTS AND DISCUSSION

Antiaromatic Holes

Aihara showed that [9]coronaphene is "marginally antisuperaromatic" which means that there is extra destabilization due to the 4n macrocyclic conjugation contribution, although the entire π system is highly aromatic [9]. In the case of [9]coronaphene ($C_{36}H_{18}$), the most important antiaromatic macrocyclic conjugation contribution out of 512 antiaromatic macrocyclic circuits is the C12 inner conjugated circuit. We refer to the inner C12 circuit as an antiaromatic hole [2].

Such an antiaromatic hole has unique attributes in graphenes. Graphenes are well-defined, nanosized polycyclic aromatic hydrocarbons having potential uses in the fabrication organic electronic devices [10]. Removal of a single carbon atom from a graphite system generates a point defect that is a one-atom hole (called a Schottky defect) [11]. Using Aihara's topological superaromatic stabilization energy (t-SSE) index, it was shown that coronoid related systems that were HMO (Hückel MO) diradicals but VB (valence-bond) nonradicals (Kekuléan systems) displayed relatively more enhanced macrocyclic antiaromatic contributions (more negative t-SSE values) [2]. We will examine a new coronoid-related example that has these characteristics associated with antiaromaticity, which also represents a new type of concealed coronoid.

A New Class of Concealed Diradical Coronoids

A concealed diradical (or even-membered radical) benzenoid hydrocarbon is defined based on the peak-to-valley difference criterion by Gordon and Davison [12]. A peak-to-valley difference of zero for a non-Kekuléan benzenoid is called a concealed or hidden radical benzenoid system; this zero difference also occurs between the number of starred and unstarred carbon vertices. An example of a concealed diradical benzenoid is Clar's goblet ($C_{38}H_{18}$) which can be constructed by joining two benzo[*cd*]pyrene monoradicals ($C_{19}H_{11}$) at their unstarred peaks (*cf*. with page 3517 in ref. 4); it has the same number of peaks as valleys but is a

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diradical. The search and study of concealed diradical benzenoid and coronoid hydrocarbons has been the subject of a number of papers [13]. Fig. (**1**) presents another type of concealed coronoid. This type of concealed diradical coronoid is an HMO diradical but a VB nonradical. The criterion for its recognition is based on McClelland's fragmentation principle [14]. Fig. (**1**) shows that the right-hand mirror fragment of this coronoid is an odd carbon monoradical and therefore by the pairing theorem the precursor coronoid must be doubly degenerate in the eigenvalues of zero and must be a concealed HMO diradical though it has a VB structure. This $C_{44}H_{20}$ coronoid is the smallest concealed HMO diradical. Using this right-hand mirror fragment, one can determine the unnormalized eigenvectors for the doubly degenerate zero eigenvalues of this coronoid given in Fig. (**2**). This same strategy was used to detect (even-membered carbon) diradical character of symmetrical indacenoids [15].

Successive Circumscribing of Conjugated Polycyclic Hydrocarbons with Hexagonal Rings

We have shown that successive circumscribing with hexagonal rings leads to certain successors having certain characteristics. The characteristic patterns that emerge upon successive circumscribing various classes of polycyclic aromatic hydrocarbons are diagnostically useful. Successive

circumscribing of benzenoids, fluorenoids/fluoranthenoids, and indacenoids leads to constant-isomer series [16]. Circumscribing of disjoint diradicals give nonradical successors whereas circumscribing nondisjoint diradicals leads to larger diradical successors; e.g., circumscribing the disjoint diradical of bisallyl (C_6H_8) gives anthanthrene ($C_{28}H_{14}$), a nonradical, and circumscribing the nondisjoint diradical of triangulene ($C_{22}H_{12}$) gives circumtriangulene diradical ($C_{52}H_{18}$). Circumscribing a concealed diradical benzenoid will eventually lead to a nonradical benzenoid. For example, circumscribing Clar's goblet ($C_{38}H_{18}$), a concealed diradical benzenoid, gives a Kekuléan $C_{80}H_{24}$ successor benzenoid. Successive circumscribing of a fluorenoid/fluoranthenoid hydrocarbon alternates from monoradical to nonradical species. Successive circumscribing of a concealed HMO diradical coronoid alternates from concealed HMO diradical to nonradical species. For example, circumscribing the $C_{44}H_{20}$ concealed HMO diradical coronoid in Fig. (**1**) gives a nonradical (Kekuléan) $C_{84}H_{26}$ coronoid and circumscribing again gives the $C_{136}H_{32}$ concealed HMO diradical shown in Fig. (**3**).

Coalescence of Antiaromatic Holes in Graphene

Fig. (**4**) shows the coalescence of two phenalenyl-shaped antiaromatic holes to form a pyrene-shaped aromatic hole. Using Benson's revised thermodynamic group additivity
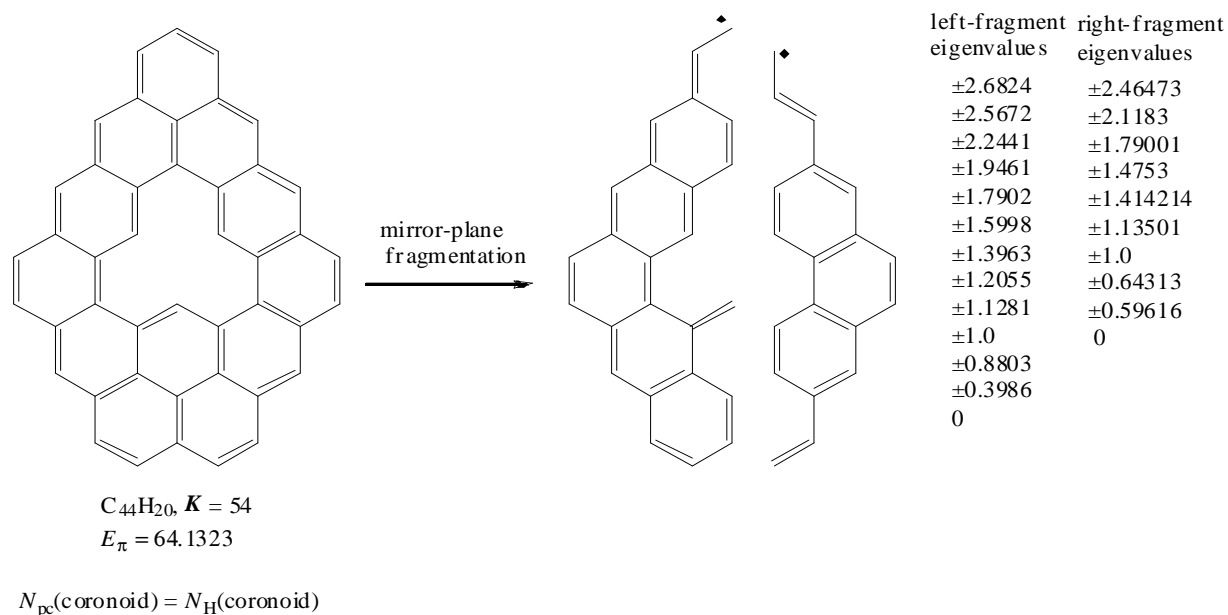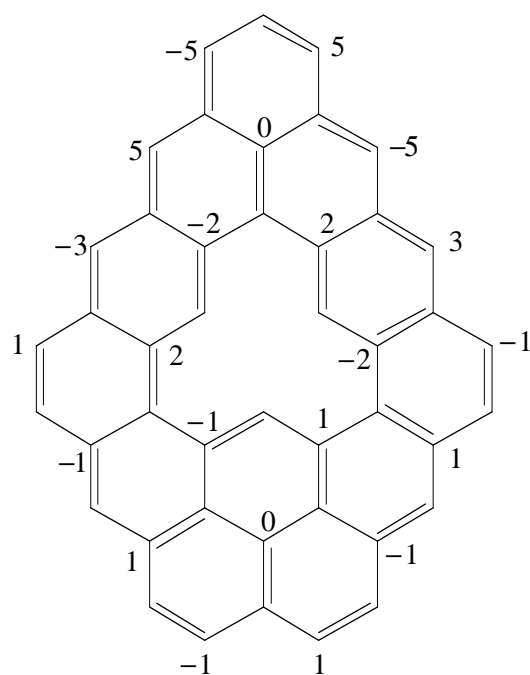

	left-fragment eigenvalues	right-fragment eigenvalues
	±2.6824	±2.46473
	±2.5672	±2.1183
	±2.2441	±1.79001
	±1.9461	±1.4753
	±1.7902	±1.414214
	±1.5998	±1.13501
	±1.3963	±1.0
	±1.2055	±0.64313
	±1.1281	±0.59616
	±1.0	0
	±0.8803	
	±0.3986	
	0	

$C_{44}H_{20}$, $K = 54$
$E_\pi = 64.1323$

$N_{pc}(coronoid) = N_H(coronoid)$

Fig. (1). An example of a Kekuléan diradical coronoid hydrocarbon. Mirror-plane fragmentation gives a right-hand fragment which is an odd alternant hydrocarbon having a zero eigenvalue. This proves that the precursor $C_{44}H_{20}$ coronoid must ba a HMO diradical.
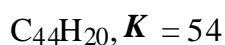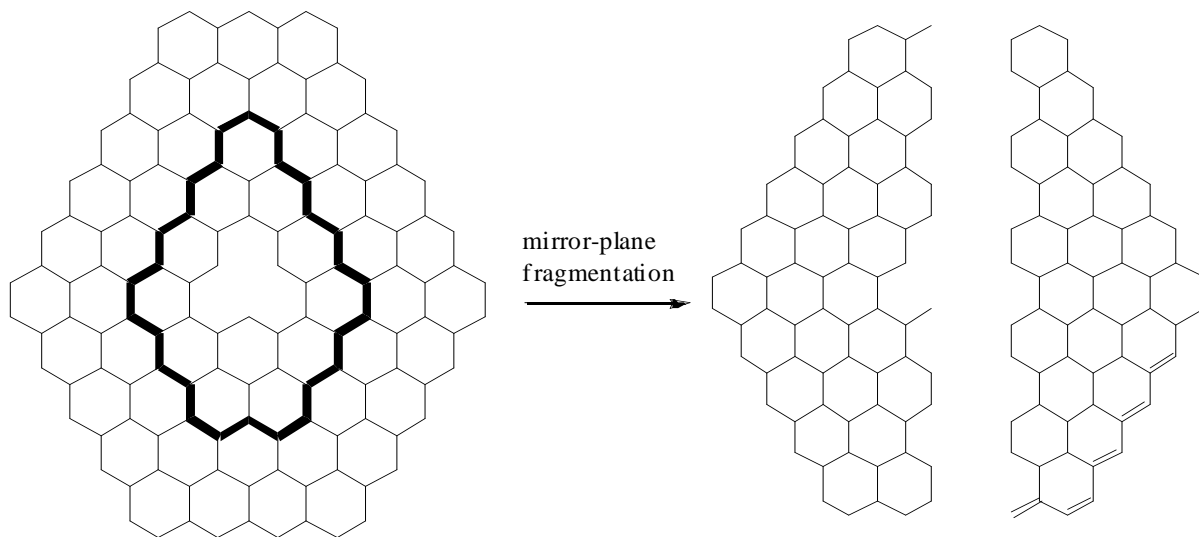
antisymmetric eigenvector

$C_{44}H_{20}, \boldsymbol{K} = 54$

Fig. (2). Eigenvectors for the doubly degenerate zero eigenvalues. Interchange signs for other orthogonal eigenvector.

mirror-plane fragmentation

Circumscribing the $C_{44}H_{20}$ coronoid shown in bold twice gives the $C_{136}H_{32}$ coronoid shown, both of which are HMO diradicals and VB nonradicals.

right-hand fragment is a C_{63} monoradical

Fig. (3). Circumscribing the $C_{44}H_{20}$ HMO diradical in Fig. (**1**) twice gives a $C_{136}H_{32}$ HMO diradical.

values [17], this process is estimated to have an ΔH(coalescence) = 51.16 kcal/mol – 97.16 kcal/mol = – 46.7 kcal/mol.

From the resonance-theoretic approach of Klein and co-workers [18], we note that if the antiaromatic holes have opposite spin polarization densities they are attracted toward each other and become canceled out in the successor aromatic hole (Fig. **4**). Alternatively, if the antiaromatic holes have the same spin polarization densities they are repelled from each other. Thus the former should have a lower energy
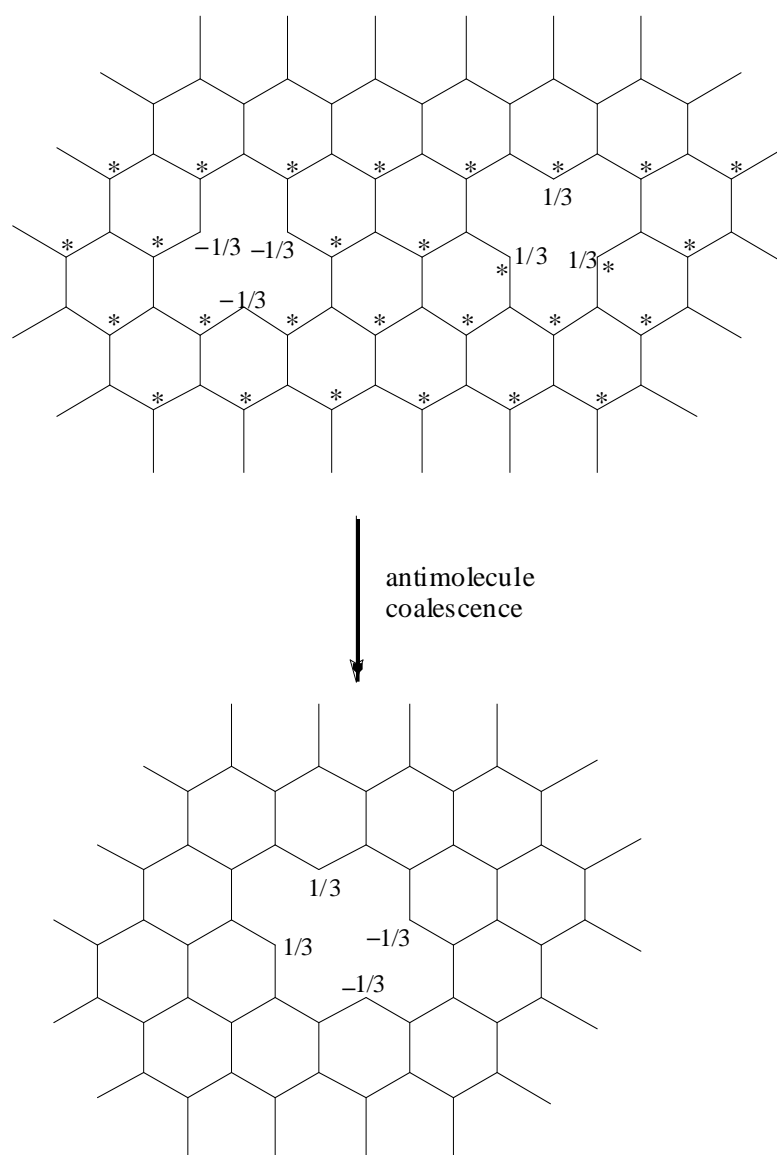
Fig. (4). Attraction and coalescence of oppositely spin polarized antiaromatic holes.

barrier than the latter though both have a thermodynamic propensity for to coalescence.

In the above mechanistic scenario, we have omitted details regarding whether the holes have dangling bonds or installed hydrogens. In the case of dangling bonds, we expect the three σ-orbitals with their electrons to be easily ionized to form a cationic cyclopropenyl aromatic-like hole. Under the influence of a magnetic field, one can visualize that the two electrons in this σ-aromatic hole and the twelve π-electrons in the antiaromatic rim should set up counter electron currents in analogy to the counter-rotating ring currents described by Fowler and coworkers [19]. With installed hydrogens, we expect the coalescence to reduce the associated steric hindrance interaction in the hole by concomitant extrusion of H_2.

CONCLUSION

We have argued that circumcoronaphene ($C_{72}H_{24}$) [2, 20], the $C_{44}H_{20}$ coronoid in Fig. (**1**) and its dicircum $C_{136}H_{32}$ successor in Fig. (**3**) represent a new type of concealed (hidden)

coronoid diradicals and have relatively more enhanced antiaromatic contributions because they are HMO diradicals though they have VB structures [2]. A model for one type of coalescence of antiaromatic holes in graphene has been suggested. The variables of antiaromaticity and spin polarization of Schottky defects need to be considered.

CONFLICT OF INTEREST

None.

ACKNOWLEDGEMENT

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