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Near omni-conductors and insulators: alternant hydrocarbons in the SSP model of ballistic conduction

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Within the SSP (source-and-sink-potential) model, a complete characterisation is obtained for the conduction behaviour of *alternant* π-conjugated hydrocarbons (conjugated hydrocarbons without odd cycles). In this model, an omni-conductor has a molecular graph that conducts at the Fermi level irrespective of the choice of connection vertices. Likewise, an omni-insulator is a molecular graph that fails to conduct for any choice of connections. We give a comprehensive classification of possible combinations of omni-conducting and omni-insulating behaviour for molecular graphs, ranked by nullity (number of non-bonding orbitals). Alternant hydrocarbons are those that have bipartite molecular graphs; they cannot be full omni-conductors or full omni-insulators, but may conduct or insulate within well-defined subsets of vertices (unsaturated carbon centres). This leads to definition of 'near omni-conductors' and 'near omni-insulators'. Of 81 conceivable classes of conduction behaviour for alternants, only 14 are realisable. Of these, nine are realised by more than one chemical graph. For example, conduction of all Kekulean benzenoids (nanographenes) is described by just two classes. In particular, the catafused benzenoids (benzenoids in which no carbon atom belongs to three hexagons) *conduct* when connected to leads *via* one starred and one unstarred atom, and otherwise *insulate*, corresponding to conduction type CII in the near-omni classification scheme.

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I. INTRODUCTION

Theoretical treatment of molecular conduction has received substantial attention for over half a century in the chemistry and physics literatures.[1–13] Sophisticated *ab initio* techniques can be applied to simulation of individual devices,[14–21] but there is a parallel tradition of devising simple models for families of devices. One attractive qualitative approach to the problem of ballistic conduction of electrons through molecules is the SSP (source-and-sink potential) model, proposed by Ernzerhof and co-workers.[22–35] In the version of SSP that incorporates Hückel (tight-binding) approximations, it gives results identical to the standard Landauer-Büttiker formula.[36,37] It has the significant advantage that it can be framed in purely graph-theoretical terms.[38–47] In chemical graph theory, vertices of the molecular graph of a π system are unsaturated C atoms, and edges are σ bonds between them. Models based on graph theory have the advantage of leading to global solutions for whole classes of molecules and giving a systematic typology[41,45] of conduction behaviour of devices. (A *device* is defined in this context by a molecular graph in which vertices $\overline{L}$ and $\overline{R}$ (in the molecule) are respectively connected to source and sink vertices L and R (outside the molecule) to represent the effect of two semi-infinite leads. *Distinct* and *ipso* devices have $\overline{L} \neq \overline{R}$ and $\overline{L} = \overline{R}$, respectively. It turns out that the transmission of a model device as a function of electron energy can be expressed in closed form in terms of four *characteristic polynomials*, those of the molecular graph and the three graphs formed by deletion of one or both of the vertices that are in contact with the external leads.[38]

This simple 'empty-molecule' version of the SSP approach, in which the ballistic electron has no interaction with the molecular electrons, has already given rise to useful generalisations such as derivations of classes of equi-conductors,[39] omni-conductors and omni-insulators,[45] and the construction of selection rules for conduction/insulation at the Fermi level that depend on counting zero roots of the structural polynomials.[41,42] Omni-conductors are molecular graphs that conduct at the Fermi level, in the SSP model, no matter which connection vertices are chosen to make the distinct (respectively, *ipso*) device. Existence of this mathematical limiting case suggests that there may be many chemical systems where conduction is insensitive to placement of contacts. Conversely, omni-insulators fail to conduct at the Fermi level for all distinct (or all *ipso*) devices. It turns out that what separates the worlds of omni-conduction and omni-insulation is *nullity*. The nullity of a graph G is the

number of zero eigenvalues in the spectrum of the graph. In chemical terms, this is exactly the number of non-bonding orbitals of the π system. A molecular graph with nullity ≤ 1 may be a distinct omni-conductor; if it has nullity ≥ 2, it may be a distinct omni-insulator.[45] This dichotomy ultimately derives from the mathematics of the interlacing theorem,[48] as deletion of two vertices of a graph can change its nullity by at most two.

The existing classifications already predict useful generalisations. However, many conjugated π systems are alternant hydrocarbons, and hence have bipartite molecular graphs (graphs for which the vertices fall into two disjoint sets such that any edges connect a vertex from each set). It follows, for example, that significant classes of conjugated hydrocarbons, such as the Kekulean benzenoids, *cannot* be distinct omni-conductors.[45] Hence, it is natural to ask how closely an alternant hydrocarbon can approach omni-conductor or omni-insulator status. The present paper gives a systematic answer to this question by defining *near* omni-conduction and insulation and showing that there are only a very few possible cases needed to describe real π systems.

The structure of the paper is as follows. The SSP model and ancillary mathematical background are described in §II, and §III defines a two-letter code classification of omni-conductors and omni-insulators, in which every alternant or non-alternant graph appears in exactly one of eight categories. This is refined in §IV to give a systematic classification of conduction/insulation behaviour of alternants in terms of a three-letter acronym (TLA) for 'near-omni' systems. We prove that of 81 conceivable cases, only 14 are realisable. §§V to VIII, supported by two mathematical appendices, show how this reduction is achieved, and give families of chemical examples (Figure 3 and TableVI). §IX describes the startingly simple restriction of the full classification for benzenoids, and §X states our overall conclusions. The end result is a complete description of ballistic conduction at the Fermi level as predicted within the SSP model.

This global picture of conduction behaviour can be used to make predictions that can be tested against more sophisticated calculations for specific devices based on systems of chemical interest, such as the benzenoids or 'nanographenes'.

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II.   THE SSP MODEL

By the SSP approach to molecular conduction we mean here the Hückel treatment of ballistic conduction of an electron of energy E through a molecule with molecular graph G connected through vertices/carbon atoms $\overline{\text{L}}$ and $\overline{\text{R}}$ to semi-infinite leads that are modelled by source and sink pseudo-atoms L and R, respectively. The behaviour of the device in this model is predicted by a generalised eigenvalue equation,[26,38] from which the resulting expression for the overall transmission T as a function of electron energy is[46]

$$T(E) = \mathcal{B}(q_\text{L}, q_\text{R}) \frac{j^2}{|D|^2}, \tag{1}$$

where

$$\mathcal{B}(q_\text{L}, q_\text{R}) = (2\beta_\text{L} \sin q_\text{L})(2\beta_\text{R} \sin q_\text{R})\beta_{\overline{\text{LL}}}^2 \beta_{\overline{\text{RR}}}^2 \tag{2}$$

is a 'band-pass' function ensuring that the electron energy is within the conduction band of each lead. The denominator is given by

$$
\begin{aligned}
D(E) = {} & \beta_\text{L} e^{-iq_\text{L}} \beta_\text{R} e^{-iq_\text{R}} s - \beta_\text{R} e^{-iq_\text{R}} \beta_{\overline{\text{LL}}}^2 t \\
& - \beta_\text{L} e^{-iq_\text{L}} \beta_{\overline{\text{RR}}}^2 u + \beta_{\overline{\text{LL}}}^2 \beta_{\overline{\text{RR}}}^2 v,
\end{aligned} \tag{3}
$$

where the polynomials s, t, u and v are to be defined below in (6), and the incoming and outgoing wavevectors q_L and q_R are functions of E satisfying the dispersion relations

$$E = \alpha_\text{L} + 2\beta_\text{L} \cos q_\text{L} = \alpha_\text{R} + 2\beta_\text{R} \cos q_\text{R}, \tag{4}$$

assuming Hückel parameters $(\alpha_\text{L}, \beta_\text{L})$ and $(\alpha_\text{R}, \beta_\text{R})$, for left and right leads. In the usual system of units, α within the molecule is set to zero, and $|\beta|$ is taken as unity. In the simplest treatment of symmetrical devices, $\alpha_\text{L} = \alpha_\text{R} = \alpha$, thus defining the Fermi level, and $\beta_\text{L} = \beta_\text{R} = \beta$.

The polynomial in the numerator satisfies the Jacobi-Sylvester relation[49]

$$j^2 = ut - sv, \tag{5}$$

where the four structural polynomials, s, t, u and v, are defined with respect to the characteristic matrix $E\mathbf{1} - \mathbf{A}$, where $\mathbf{A}$ is the adjacency matrix of the molecular graph (that is, the matrix with entries 1 for each vertex pair connected by a σ bond, and 0 elsewhere,

which is the Hückel Hamiltonian, expressed in the α, β units described above), by

$$s = \det\left(E\mathbf{1} - \mathbf{A}\right),$$
$$t = \det\left(E\mathbf{1} - \mathbf{A}\right)^{[\overline{\mathrm{L}},\overline{\mathrm{L}}]},$$
$$u = \det\left(E\mathbf{1} - \mathbf{A}\right)^{[\overline{\mathrm{R}},\overline{\mathrm{R}}]},$$
$$v = \det\left(E\mathbf{1} - \mathbf{A}\right)^{[\overline{\mathrm{LR}},\overline{\mathrm{LR}}]}. \tag{6}$$

corresponding to characteristic polynomials of the molecular graph G, and the vertex-deleted graphs $G-\overline{\mathrm{L}}$, $G-\overline{\mathrm{R}}$, $G-\overline{\mathrm{L}}-\overline{\mathrm{R}}$, respectively. The polynomial $\jmath$ can be calculated directly[38] as

$$\jmath = (-1)^{\overline{\mathrm{L}}+\overline{\mathrm{R}}}\det\left(E\mathbf{1} - \mathbf{A}\right)^{[\overline{\mathrm{L}},\overline{\mathrm{R}}]}. \tag{7}$$

In these equations, superscripts indicate the rows and columns that correspond to connection atoms $\overline{\mathrm{L}}$ and/or $\overline{\mathrm{R}}$ and are to be removed from the characteristic matrix. Reduced quantities $\hat{t}$, $\hat{u}$, $\hat{v}$ and $\hat{\jmath}$ are defined as t/s, u/s, v/s and $\jmath/s$, respectively. These reduced forms are useful in what follows.

As described below, we have used two approaches for obtaining information about systematics of conduction in the SSP model. One is suitable for formal algebraic proofs, and the other for numerical calculation. The first approach is via *selection rules*, the second through *spectral expansions*. In the first approach, conduction at the Fermi level is defined by a set of selection rules based on the numbers of zero roots of the five polynomials s, t, u, v and $\jmath$, which we will denote by g_s, g_t, g_u, g_v and g_j. The first four polynomials define nullities of the graphs G, $G-\overline{\mathrm{L}}$, $G-\overline{\mathrm{R}}$ and $G-\overline{\mathrm{L}}-\overline{\mathrm{R}}$, respectively. Devices fall into 14 cases, which reduce to the eight possibilities listed in Table I when the graph G is bipartite.[42,45] It is useful to express these rules in terms of the types of vertex involved, which we call *core* and *core-forbidden*: if the molecular graph has non-zero nullity, a *core vertex* (CV) has a non-zero entry in some eigenvector belonging to the nullspace; all other vertices are *core-forbidden* (CFV). Deletion of a CV always reduces the nullity by one. Deletion of a CFV of a bipartite graph raises the nullity by one, as CFV in this case are 'upper'.[50] The rules are exploited below to provide proofs of conduction properties.

For numerical calculation of conduction/insulation, however, it turns out to be useful to

Kind	Rule	g_t	g_u	g_v	g_j	$T(0)$
CFV+CFV	D1	g_s+1	g_s+1	g_s+2	$\geq g_s+1$	$=0$
	D2	g_s+1	g_s+1	g_s	g_s	$\neq 0$
CFV+CV	D5	g_s+1	g_s-1	g_s	$\geq g_s$	$=0$
CV+CV	D9	g_s-1	g_s-1	g_s	g_s-1	$\neq 0$
	D11.1	g_s-1	g_s-1	g_s-2	g_s-1	$=0$
	D11.2	g_s-1	g_s-1	g_s-2	$\geq g_s$	$=0$
CFV	I1	g_s+1			g_s+1	$=0$
CV	I3	g_s-1			g_s-1	$\neq 0$

TABLE I. Selection rules for Fermi-level conduction of molecular devices based on bipartite graphs with nullity g_s. Combinations of CV and CFV describe the $(\overline{\text{L}}, \overline{\text{R}})$ pair in terms of core and core-forbidden vertices (see text). Each signature $\{g_t, g_u, g_v, g_j\}$ leads to a prediction about transmission at the Fermi level, $T(0)$, as either $\neq 0$ (conduction), or 0 (insulation). Rules are labelled D for *distinct* devices ($\overline{\text{L}} \neq \overline{\text{R}}$) and I for *ipso* devices ($\overline{\text{L}} = \overline{\text{R}}$).

calculate the structural polynomials via their *spectral expansions*. For $\hat{t}$, $\hat{u}$ and $\hat{j}$, these are[46]

$$\hat{t}(E) = \sum_{i=1}^{n} \frac{(c_{\overline{\text{L}}}^i)^2}{E - E_i},$$
$$\hat{u}(E) = \sum_{i=1}^{n} \frac{(c_{\overline{\text{R}}}^i)^2}{E - E_i},$$
$$\hat{j}(E) = \sum_{i=1}^{n} \frac{c_{\overline{\text{L}}}^i c_{\overline{\text{R}}}^i}{E - E_i}, \tag{8}$$

where $\{E_i\}_{i=1,\dots,n}$ are the eigenvalues of the adjacency matrix of the molecular graph and c_{p}^i is the entry (assumed, without loss of generality, to be real) for vertex p of the molecular graph in the ith eigenvector. Connection vertices are $\text{p} = \overline{\text{L}}, \overline{\text{R}}$. In the ordering convention that the first g_s eigenvectors belong to the nullspace ($E_i = 0$), each polynomial can be split

into two sums that differ in explicit dependence on E:

$$\hat{t}(E) = \sum_{i=1}^{g_s} (c_{\overline{L}}^i)^2 E^{-1} + \sum_{i=g_s+1}^{n} \frac{(c_{\overline{L}}^i)^2}{E - E_i} = \hat{t}_b E^{-1} + \hat{t}_a,$$

$$\hat{u}(E) = \sum_{i=1}^{g_s} (c_{\overline{R}}^i)^2 E^{-1} + \sum_{i=g_s+1}^{n} \frac{(c_{\overline{R}}^i)^2}{E - E_i} = \hat{u}_b E^{-1} + \hat{u}_a,$$

$$\hat{j}(E) = \sum_{i=1}^{g_s} c_{\overline{L}}^i c_{\overline{R}}^i E^{-1} + \sum_{i=g_s+1}^{n} \frac{c_{\overline{L}}^i c_{\overline{R}}^i}{E - E_i} = \hat{j}_b E^{-1} + \hat{j}_a. \tag{9}$$

Likewise, the reduced polynomial for the two–vertex deleted graph, $\hat{v}(E)$, splits into three:

$$\hat{v}(E) = \hat{v}_c E^{-2} + \hat{v}_b E^{-1} + \hat{v}_a, \tag{10}$$

where

$$\hat{v}_a = (\hat{u}_a \hat{t}_a - \hat{j}_a^2),$$
$$\hat{v}_b = (\hat{u}_a \hat{t}_b + \hat{u}_b \hat{t}_a - 2\hat{j}_a \hat{j}_b),$$
$$\hat{v}_c = (\hat{u}_b \hat{t}_b - \hat{j}_b^2). \tag{11}$$

For $g_s = 1$, $\hat{v}_c$ is zero; for $g_s = 0$, only $\hat{t}_a$, $\hat{u}_a$, $\hat{j}_a$ and $\hat{v}_a$ are present. Assignment of cases to conduction or insulation at the Fermi level according to Table I can be made through computation of terms in the expansions at $E = 0$. The seven conditions for conduction and seven for insulation[45] for a device with $(p, q) = (\overline{L}, \overline{R})$, ranked by nullity g_s, are given in Table II.

III.   OMNI-CONDUCTION AND OMNI-INSULATION

For general graphs, we have defined possible conduction behaviours for the set of devices derived from a given graph.[45] An *omni-conductor* conducts at the Fermi level for all possible devices of a given type: *distinct* omni-conductors conduct for all $\overline{L} \neq \overline{R}$; *ipso* omni-conductors conduct for all $\overline{L} = \overline{R}$; *strong* omni-conductors conduct for all $\overline{L}, \overline{R}$. An *omni-insulator* has the converse behaviour; it has *zero* conduction at the Fermi level for all possible devices of the given type: *distinct* omni-insulators insulate for all $\overline{L} \neq \overline{R}$; *ipso* omni-insulators insulate for all $\overline{L} = \overline{R}$; it turns out that *strong* omni-insulators do not exist[45].

A systematic typology of omni-conductors and omni-insulators by nullity can be derived[45] and is illustrated in Table III. In the form shown, this classification has some useful features and some limitations. The terminology of distinct/*ipso* conduction/insulation patterns

Nullity	Conduction	Insulation
$g_s = 0$ $\hat{j}_a \neq 0$		$\hat{j}_a = 0$
$g_s = 1$	$\hat{j}_b \neq 0$ $\begin{cases} \hat{u}_b + \hat{t}_b \neq 0 \\ \text{or} \\ \hat{v}_b \neq 0 \end{cases}$ or $\hat{j}_b = 0$ and $\hat{j}_a \neq 0$ and $\hat{u}_b + \hat{t}_b = 0$ and $\hat{v}_b = 0$	$\hat{j}_b = 0$ and $\hat{j}_a = 0$ or $\hat{j}_b = 0$ and $\hat{j}_a \neq 0$ $\begin{cases} \hat{u}_b + \hat{t}_b \neq 0 \\ \text{or} \\ \hat{v}_b \neq 0 \end{cases}$
$g_s > 1$	$\hat{v}_c = 0$ and $\hat{j}_b \neq 0$ $\begin{cases} \hat{u}_b + \hat{t}_b \neq 0 \\ \text{or} \\ \hat{v}_b \neq 0 \end{cases}$ or $\hat{v}_c = 0$ and $\hat{j}_b = 0$ and $\hat{j}_a \neq 0$ and $\hat{u}_b + \hat{t}_b = 0$ and $\hat{v}_b = 0$	$\hat{v}_c \neq 0$ or $\hat{v}_c = 0$ $\begin{cases} \hat{j}_b = 0 \text{ and } \hat{j}_a \neq 0 \text{ and } \hat{v}_b \neq 0 \text{ or } \hat{u}_b + \hat{t}_b \neq 0 \\ \text{or} \\ \hat{j}_b = 0 \text{ and } \hat{j}_a = 0 \end{cases}$

TABLE II. The seven conditions for device conduction (left) and the seven for insulation (right). Note; two misprints in the equivalent tables in Ref. 45 have been corrected here. These were in the last line of Conduction with $g_s = 1$, and middle line of Insulation with $g_s > 1$.

allows identification of families of molecular graphs with specific conduction behaviour.[45] However, the categories are not mutually exclusive. For example, K_2, the molecular graph of ethene, is both a distinct omni-conductor and an *ipso* omni-insulator. A more extensive scheme in which every molecular graph has exactly one home is illustrated by the Venn diagram in Figure 1. The idea is to employ a two-letter code for each possible combination of distinct and *ipso* behaviour. The alphabet of possibilities, { C, I, X }, denotes omni-conduction, omni-insulation, or mixed conduction/insulation within a specified set; the first letter of the code describes the set of distinct devices associated with a given graph, and the second the set of *ipso* devices. X is taken to mean 'not C or I' in the unique case of K_1, the isolated π centre, where there are no distinct pairs. Of the nine combinations, all but II (strong omni-insulators) have examples amongst chemical graphs. Combination of the codes with the separation into three nullity types gives the 27 categories listed in Table IV, of which 14 are empty and the remaining 13 are realised by small graphs. This enlarged classification gives a template for the treatment of bipartite molecular graphs.

Not all cases listed in Tables III and IV are realisable for bipartite graphs and in fact, as will be proved below, only five two-letter codes apply to bipartite graphs (XI ($\eta = 0$), XC, XX ($\eta \geq 1$), IC, IX ($\eta > 1$)). The main business of the present investigation is to work out how to translate the restrictions imposed by bipartivity into a full classification of Fermi-level conduction behaviour of bipartite molecular graphs (alternant π systems).

IV. A CLASSIFICATION SCHEME FOR ALTERNANT HYDROCARBONS

Evidently, a more refined classification is needed to capture the conduction behaviour of devices based on alternant hydrocarbons. The molecular graph of an alternant hydrocarbon is *bipartite*. By definition, the vertices of a bipartite graph can be split into two disjoint partite sets, which we may call starred and unstarred, and denote by V_1 and V_2, respectively, with $|V_1| \geq |V_2|$. K_1 is trivially bipartite, with V_2 empty. Each edge of the graph connects a starred and an unstarred vertex. Bipartite graphs are precisely those graphs that contain no odd cycles. Conduction behaviour is affected by these properties.

The classification adopted here concentrates on behaviour within and between partite sets. The distinct/*ipso*/strong classification for general graphs is replaced by a set of three-

Conduction behaviour	Nullity		
	0	1	≥ 2
Distinct omni–conductor	Some	Nut	None
Ipso omni–conductor	Some	Some	Some
Strong omni–conductor	Some	Nut	None
Distinct omni–insulator	None	None	Some
Ipso omni–insulator	Some	None	None
Strong omni–insulator	None	None	None

TABLE III. Classification of conduction behaviour by nullity for general connected graphs.[45] 'None' indicates conduction types unrealisable by connected graphs. 'Some' indicates that graphs with given type and nullity exist. Of nine realisable conduction classes, two (denoted 'Nut') are exactly nut graphs. A *nut graph* has nullity one and consists entirely of core vertices (CV); all non-trivial nut graphs are non-bipartite.[51]

Code	Nullity		
	0	1	≥ 2
CC	Some	Nut	None
CI	Some	None	None
CX	Some	None	None
IC	None	None	Some
II	None	None	None
IX	None	None	Some
XC	Some	Some	Some
XI	Some	None	None
XX	Some	Some	Some

TABLE IV. Full classification of conduction behaviour by nullity for general connected graphs. Conventions as in Table III.

letter acronyms (TLA). The alphabet is {C, I, X}, as with the two-letter codes, and the three sets of interest for bipartite graphs are indicated by position: the first letter refers to *inter* devices (one starred and one unstarred connection vertex), the second to *intra* (two starred or two unstarred connection vertices) and the third to *ipso* (connection via a single vertex). X is interpreted as 'neither C nor I', so that it can also be used when the set in
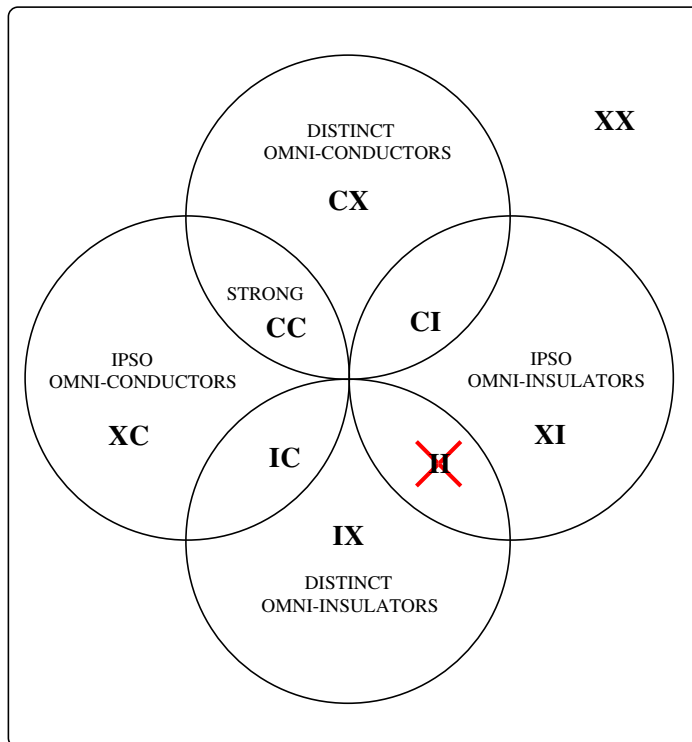
FIG. 1. Venn diagram showing the relationship between the overlapping classes of conductors and insulators shown in Table III and the new disjoint classification given in Table IV. The red cross for category II indicates the impossibility of strong omni-insulators.

question is empty, as for *intra* and *inter* sets for K_1, and the *intra* set for K_2.

Thus, for example, a TLA of CIX would imply omni-conduction for all distinct pairs $\overline{L} \neq \overline{R}$ from opposite sets, omni-insulation for all pairs $\overline{L} \neq \overline{R}$ of the same set, and mixed conduction/insulation for *ipso* devices.

There are 27 three-letter codes to be considered, from CCC to XXX. Guided again by the significance of nullity in classification for general graphs, we distinguish cases with nullities $\eta = 0, 1, \geq 2$, leading to a total of 81 combinations of TLA code and nullity. We check each of these to decide whether a given combination of TLA and nullity is possible (and find a small bipartite graph example), or can be proved to be impossible.

V. CALCULATIONS

As a preliminary, assessments were carried out for sets of graphs using the numerical approach for calculation of spectral expansions of the structural polynomials. Complete

sets of bipartite graphs on up to 10 vertices, bipartite chemical graphs (connected bipartite graphs with maximum degree 3) on up to 12 vertices, and benzenoids on up to 12 hexagons, all available from previous work,[45] were tested. These calculations provided examples for 14 of the 81 TLA/nullity combinations. Figure 2 shows the smallest graphs for each of the 14 combinations. In all but one case these are chemical graphs (skeletons of possible alternant hydrocarbons).
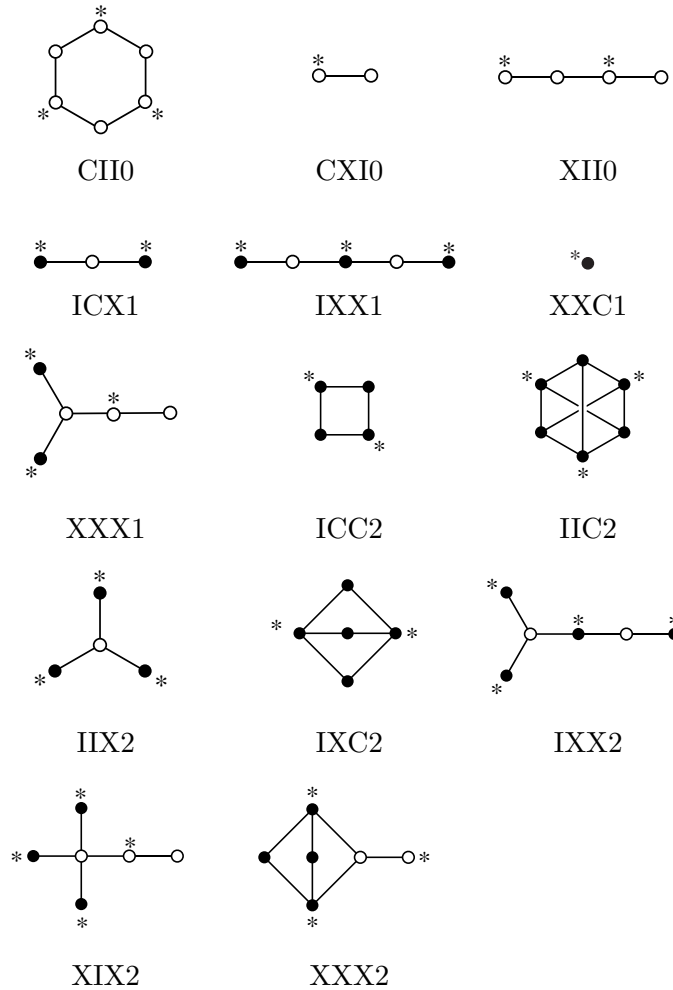

FIG. 2. Smallest examples of the 14 conduction types for devices based on bipartite graphs, named by three-letter acronym and nullity). Vertices in the partite sets V_1 and V_2 are shown as starred and unstarred, respectively. Core vertices are indicated with black-filled circles, and core-forbidden vertices with white-filled circles, respectively.

VI. ELIMINATION OF REMAINING CASES

The grid of 81 combinations is shown in Table V. We begin by populating the table with the cases where we have an example from exhaustive search of small graphs. These cells are filled with the string 'Some'. The focus of the theoretical work is then to eliminate as many as possible of the remaining cells. The conjecture is that all other cells correspond to combinations that are impossible for bipartite graphs.

We can immediately eliminate some combinations using the old broad classification of possible and impossible cases for general graphs. Strong omni-insulators are not possible.[45] Hence type III can be ruled out for bipartite graphs. Similarly, as distinct and strong omni-conductors for nullity one are identical with the class of nut graphs[51] (graphs with $n > 1$ and $\eta = 1$ in which the eigenvector of zero eigenvalue has no zero entries), and as nut graphs are not bipartite,[51] types CCC and CCI are ruled out for nullity one.

Impossibility proofs for all those combinations left open by the computer search are briefly indicated in Appendix A. The results of the proof procedure are summarised in Table V, from which it is evident that the conjecture was correct: we do now have the *complete* classification of possibilities.

Application: As an essentially graph-theoretical approach, the SSP model gives predictions for general classes of alternant hydrocarbons. Figure 3 illustrates representative families of bipartite molecular graphs. Table VI lists the SSP predictions for their conduction behaviour.

VII. RARE CASES

Some cases in Table V correspond to a very small number of graphs.

A. Cases CXI, ICX and XXC

Types CXI, ICX and XXC have only one example each within the test sets; the only graph found for XXC is K_1, the molecular graph of a single unsaturated carbon centre; CXI is K_2, the complete graph on two vertices and the molecular graph of ethene; the only graph found for ICX is P_3, the path on three vertices, the molecular graph of the allyl radical. As shown in Appendix A, these three graphs are the unique examples of their respective
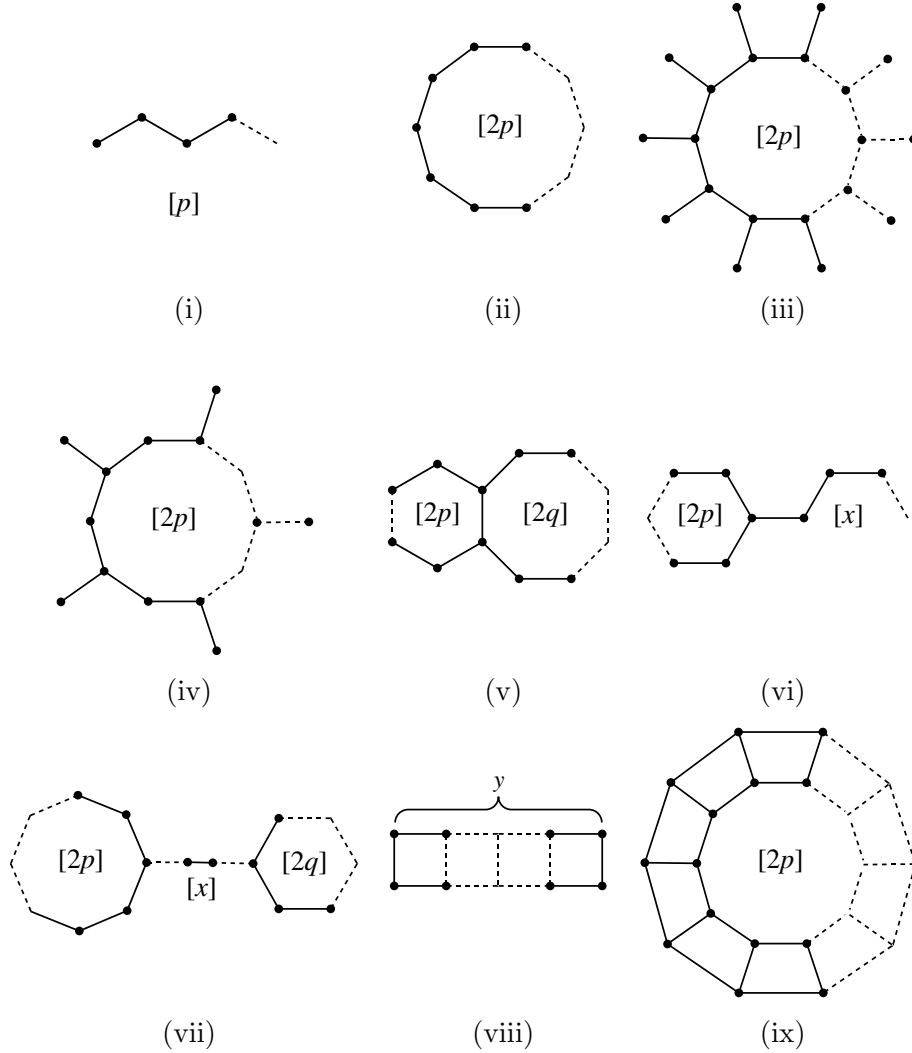
FIG. 3. Families of bipartite graphs with systematic conduction behaviour in the SSP model. the families are: (i) paths (linear polyenes); (ii) cycles (annulenes); (iii) radialenes; (iv) semi-radialenes; (v) bi-cycles (fused annulenes); (vi) tadpoles; (vii) bowties; (viii) ladders; (ix) prisms. Cycle sizes in bipartite graphs are even, and denoted here by $2p$ or $2q$; x is the number of atoms in a chain connected to a cycle, not counting vertices common to the chain and a cycle; y is the number of squares in the ladder. See Table VI for the results.

conduction types.

B. Case IIC

The search found only one example amongst chemical graphs for type IIC, although it found others within non-chemical graphs. The sole chemical graph is $K_{3,3}$. This is a *complete*

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Case	Nullity, η			Case	Nullity, η			Case	Nullity, η		
	0	1	> 1		0	1	> 1		0	1	> 1
CCC	0:1, 0:2	1:1, 1:3	2:3, 2:4	ICC	0:1, 0:2	1:1	Some	XCC	0:1, 0:2	1:1	2:4
CCI	0:2	1:1, 1:3	2:1, 2:3	ICI	0:2	1:1	0:1, 2:1	XCI	0:2	1:1	2:1
CCX	0:1, 0:2	1:3, 1:4	2:2, 2:3	ICX	0:1, 0:2	P_3	2:2	XCX	0:1, 0:2	1:4	2:2
CIC	0:1	1:1, 1:2, 1:3	2:3, 2:4	IIC	0:1	1:1, 1:2	Some	XIC	0:1	1:1, 1:2	2:4
CII	Some	1:1, 1:2, 1:3	2:1, 2:3	III	0:3	1:1, 1:2	2:1	XII	Some	1:1, 1:2	2:1
CIX	0:1	1:2, 1:3	2:3	IIX	0:1	1:2	Some	XIX	0:1	1:2	Some
CXC	0:1, 0:2	1:1, 1:3	2:3, 2:4	IXC	0:1, 0:2	1:1	Some	XXC	0:1, 0:2	K_1	2:4
CXI	K_2	1:1, 1:3	2:1, 2:3	IXI	0:2	1:1	2:1	XXI	0:2	1:1	2:1
CXX	0:1, 0:2	1:3	2:3	IXX	0:1, 0:2	Some	Some	XXX	0:1, 0:2	Some	Some

TABLE V. Conduction behaviour of alternant π-conjugated hydrocarbons. showing the existence status of all 81 conceivable combinations of *inter-intra-ipso* device behaviour with nullity of the molecular graph. Entries 'Some' indicate that at least one example has been found. Entries in the form η:number refer to the theorems that can be used to rule out a given case (see Appendix A for details). Cases CXI ($\eta = 0$), XXC and ICX ($\eta = 1$) and IIC ($\eta > 1$) are each realised by only one chemical graph. These are $K_2 \equiv K_{1,1}$, K_1, $P_3 \equiv K_{2,1}$ and $K_{3,3}$, respectively. Case IIC also has non-chemical realisations; no chemical realisation has been found so far for case XIX.

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Family	Sub-family	Nullity	TLA
Path	K_1	1	XXC
	K_2	0	CXI
	P_3	1	ICX $\rightarrow$ ICci
	Even path, $n > 2$	0	XII
	Odd path, $n > 3$	1	IXX $\rightarrow$ Icici
Cycle	$2p = 4N + 2$	0	CII
	$2p = 4N$	2	ICC
Radialene	all p	0	XII
Semi-radialene	$2p = 4$	2	IXX $\rightarrow$ Iixci
	$2p > 4$	p	IIX $\rightarrow$ IIci
Bi-cycle	$2p = 4N + 2, 2q = 4N' + 2$	0	CII
	all others	0	XII
Tadpole	$2p = 4N + 2, x = 2N'$	0	XII
	$2p = 4N + 2, x = 2N' + 1$	1	IXX $\rightarrow$ Icici
	$2p = 4N, x = 2N'$	2	IXX $\rightarrow$ Icxcx
	$2p = 4N, x = 2N' + 1$	1	XXX $\rightarrow$ Xixix
Bowtie	$2p = 4N + 2, 2q = 4N' + 2, x = 2N''$	0	XII
	$2p = 4N + 2, 2q = 4N' + 2, x = 2N'' + 1$	1	IXX $\rightarrow$ Icici
	$2p = 4N + 2, 2q = 4N', x = 2N''$	2	IXX $\rightarrow$ Icxcx
	$2p = 4N + 2, 2q = 4N', x = 2N'' + 1$	1	XXX $\rightarrow$ Xixix
	$2p = 4N, 2q = 4N', x = 2N''$	2	XXX
	$2p = 4N, 2q = 4N', x = 2N'' + 1$	3	IXX $\rightarrow$ Icxcx
Ladder	$y = 3N + 1, N > 1$	2	IXX
	$y \neq 3N + 1$	0	XII
Prism	$2p = 6N$	4	IXC
	$2p \neq 6N$	0	CII

TABLE VI. Conduction behaviour for families of bipartite molecular graphs. n is the number of vertices; p, q and x are as defined in Figure 3, where $2p$ and $2q$ are the cycle sizes and x is the length of a chain of vertices that are not in any cycle. Three-letter acronyms are defined in section IV; expanded five-letter acronyms are defined in section VIII.

bipartite graph. It has three starred and three unstarred vertices, and all starred are joined

to all unstarred vertices; it appears in mathematical puzzles as the 'Utility Graph' In a complete bipartite graph, $K_{p,q}$, each of the p vertices in V_1 is joined by an edge to each of the q vertices in V_2. $K_{3,3}$ is famously non-planar (cannot be drawn in the plane without edges crossing, in chemistry it appears as the graph of the discarded Claus proposal for the structure for benzene, where antipodal carbon atoms were connected by extra single bonds.[?]

Other examples of (non-chemical) graphs in type IIC are constructed in Appendix B.

C. Case XIX

Another rare case is XIX. In the computer search, no chemical graph was found for this type, although non-chemical graphs such as the six-vertex Latin Cross are found in this class (See the entry for XIX in Figure 2).

VIII. REFINING THE TLA DESCRIPTION

The three-letter classification can be further refined in some cases. In the *intra* and *ipso* positions of the TLA, a letter X could signify conduction within one partite set and insulation within the other, or conduction or insulation in one set and mixed possibilities in the other, and so on. In some cases, further reasoning allows the letter X to be replaced by a more detailed specification, and we use two lower-case letters such as ci, cx, ix to indicate the behaviour within V_1 and V_2. The core and core-forbidden classification of vertices used earlier is also useful here.

A. Singular bipartite graphs with $\eta = 1$

For graphs with nullity zero, all vertices are CFV, *inter* and *intra* pairs (if any) are all of kind CFV-CFV, and no new interesting cases arise from distinguishing V_1 and V_2.

For graphs with nullity one, all core vertices are in the larger partite set V_1, and the interesting case is when V_1 is 'full', i.e. when every member of V_1 is CV. V_2 is 'empty' in the sense that every vertex in V_2 is CFV. A graph with this distribution of CV and CVF is a *half-core*. If G is a half-core with $\eta = 1$, the *intra* pairs in V_1 are CV/CV and satisfy D9. For *intra* pairs in V_2 we have CFV/CFV, and potentially Rules D1 or D2. However, repeated

removal of vertices raises the nullity at each step, as the difference $||V_1| - |V_2||$ increases by one at each step. Hence, the CFV/CFV pairs are insulating, by Rule D1. Therefore, the expanded code has ci instead of X in the *intra* position. The *ipso* entry is also ci (by I1 and I3), whereas the *inter* pairs are all insulating, by D5. Hence, all half-cores with $\eta = 1$ have TLA IXX and expanded code Icici.

B. Singular bipartite graphs with $\eta > 1$

For graphs with nullity two or more, the potentially interesting cases are half-cores, defined as above, and *cores*, in which all vertices are CV so that both V_1 and V_2 are full.

If the graph is a *half-core* with $\eta \geq 2$, the *ipso* entry X is equivalent to ci. The *inter* entry is I (all *inter* pairs fall under Rule D5). Therefore the conduction types of interest are IIX or IXX. The type IIX is simply expanded to IIci, and hence is resolved. However, experimentation shows that graphs in IXX can be Ixici, so this type is not fully resolved.

If the graph is a *core* with $\eta \geq 2$, the *ipso* entry is C (all vertices are CV), and hence the only unresolved entry is IXC. Some small graphs can be found that correspond to IxxC, so this case is unresolved. In summary, the expanded codes give complete resolution for $\eta = 1$ but only partial resolution for $\eta = 2$.

IX. BENZENOIDS

Calculations on all benzenoids on up to twelve hexagonal rings are summarised in Table VII. Here, benzenoids are taken to be simply-connected subgraphs of the graphene plane composed of hexagonal rings only. In a *catafused* benzenoid all vertices are in the perimeter, i.e. no vertices belong to three hexagons. Conversely, all *perifused* benzenoids have at least one such 'internal' vertex. The table reveals some interesting patterns of predicted conduction behaviour between these classes of benzenoids. It turns out that only four TLA are needed to describe the conduction behaviour of all benzenoids in the range that we searched, two for those with Kekulé structures, and two for those without.

| N_{hex} | $\eta = 0$ | | | $\eta = 1$ | | $\eta \geq 2$ | | N_{tot} |
| | Cata | Peri | | Peri | | Peri | | |
	CII	CII	XII	IXX	XXX	IXX	XXX	
1	1							1
2	1							1
3	2				1			3
4	5		1	1				7
5	12	1	2	5	2			22
6	36	7	8	27	1	2		81
7	118	33	39	121	13	7		331
8	411	160	193	586	33	52		1435
9	1489	787	947	2776	181	322	3	6505
10	5572	3756	4779	13097	927	1931	24	30086
11	21115	17557	24207	61627	5419	11096	208	141229
12	81121	81314	122483	290133	30726	62247	1560	669584

TABLE VII. Conduction behaviour of benzenoids, classified by nullity. For the non-singular benzenoids ($\eta = 0$), the first CII column corresponds to catafused benzenoids; the second CII and first XII columns correspond to Kekulean perifused benzenoids. All benzenoids with $\eta > 0$ are perifused. N_{tot} is the total number of benzenoids with N_{hex} rings.

A. Kekulean benzenoids

A benzenoid is *Kekulean* if it has a perfect matching (Kekulé structure). A benzenoid is Kekulean if and only if it is non-singular ($\eta = 0$).[52] The perimeter of a catafused benzenoid is a Hamiltonian circuit (a circuit of edges that visits every vertex exactly once) and therefore every catafusene has at least two perfect matchings. Hence, all catafused benzenoids are Kekulean. In contrast, perifused benzenoids may be Kekulean or non-Kekulean.

Kekulean benzenoids fall into conduction types CII and XII (Table V), as they are non-singular bipartite graphs $G \neq K_2$. However, the numbers in Table VII suggest a further conjecture, that *all* catafused benzenoids correspond to type CII, whereas perifused Kekulean benzenoids may belong to *either* CII or XII.

This conjecture is straightforwardly proved. First, *ipso* and *intra* entries in the TLA for a catafused benzenoid G are both I, by Theorems 0:1 and 0:1 (Appendix A). The *inter*

entry of the TLA is fixed by the analysis illustrated in Figure 4. An *inter* pair of connection vertices has one vertex in V_1, say $\overline{\text{L}}$, and one, say $\overline{\text{R}}$ in V_2 (Figure 4(a)). The two vertices are connected along the perimeter by two paths that consist of an odd number of edges (Figure 4(b)). Choose one of the paths and call it P_1. Now choose the matching of the perimeter circuit in which P_1 has two terminal double bonds, and call that matching M_1. The complementary perimeter matching is M_2, with terminal double bonds in the other path, P_2 (Figure 4(c)). Now delete vertices $\overline{\text{L}}$ and $\overline{\text{R}}$. The path $P_1 - \overline{\text{L}} - \overline{\text{R}}$ has a perfect matching when its edges are chosen as in M_2, as does path $P_2 - \overline{\text{L}} - \overline{\text{R}}$ when its edges are chosen as in M_1 (see Figure 4(d). Hence the graph $G - \overline{\text{L}} - \overline{\text{R}}$ has a perfect matching in which any remaining chordal edges carry single bonds. As any internal face remaining in this two-vertex-deleted graph is still of size $4N + 2$, the existence of this perfect matching implies nullity zero.[52–54] Therefore, all *inter* pairs of a catafused benzenoid obey Rule D2, and the conduction type is CII. This proof also applies to catafused helicenes. In contrast, non-singular perifused benzenoids may be either CII or XII; the smallest examples of each type are illustrated in Figure 5(a) and (b).

B. Non-Kekulean benzenoids

The remaining columns of Table VII deal with non-Kekulean benzenoids. Benzenoids with $\eta \geq 1$ are found in conduction types IXX and XXX, as they must be, since P_3 is not a benzenoid. However, the same two TLAs apparently suffice also for benzenoids with $\eta \geq 2$: specifically, the five other types available to general bipartite graphs (ICC, IIC, IIX, IXC, XIX) are not found for benzenoids in the range of the search. This may be an effect of small numbers; we are not yet aware of a proof of the sufficiency of the two classes for benzenoids with $\eta > 1$.

We note that a half-core benzenoid is of type Icici (hence also IXX). All IXX entries in the table for $\eta = 1$ and for $\eta > 1$ correspond to half cores; it would be interesting to know if this observation generalises.

Figure 5(c) and (d) show the smallest examples of benzenoids with $\eta = 1$. The smallest benzenoid with $\eta = 1$ is phenalene (Figure 5(c)); the central vertex carries entry zero in the NBO, leading to conduction type XXX (Xixix). The smallest half core with $\eta = 1$ is benzophenalene (Figure 5(d)).
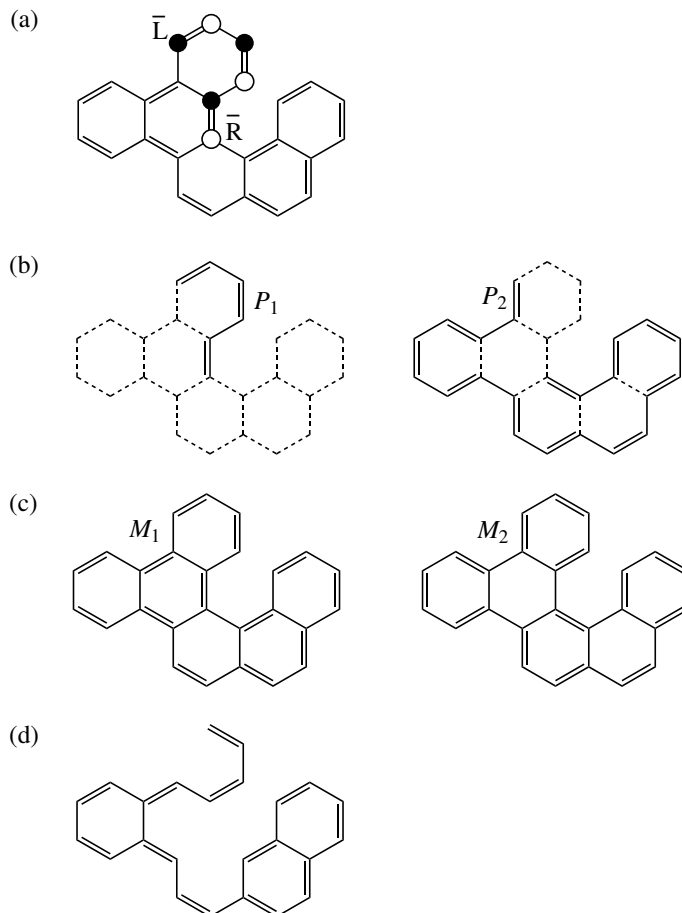
FIG. 4. Pictorial proof that catafused benzenoids all belong to conduction type CII. (a) A cata-fusene G with an *intra* pair of connections $\overline{\mathrm{L}}$ and $\overline{\overline{\mathrm{R}}}$; (b) Two perimeter paths P_1 and P_2 connecting $\overline{\mathrm{L}}$ and $\overline{\overline{\mathrm{R}}}$; (c) The pairs of perimeter perfect matchings M_1 and M_2, chosen to given terminal double bonds in paths P_1 and P_2, respectively; (d) Matching of the vertex-deleted graph $G-\overline{\mathrm{L}}-\overline{\overline{\mathrm{R}}}$, proving that the device is a conductor by Rule D2.

Phenalene is also the smallest of the triangulenes, which as the name suggests consist of a triangular array of hexagons and hence of $1, 3, 6, \cdots a(a+1)/2$ hexagons, where a is the number of rows and $a(a+1)/2$ is the total number of hexagons. As neutral molecules, and in a high-spin ground state, the triangulenes with $a > 1$ would have η unpaired spins distributed over vertices of set V_1. For $a > 2$, $\eta > 1$ the system is a half-core, and hence of type IXX (in fact, Iixix). The case $a = 2$, $\eta = 1$ (phenalene) is special in having a CFV in the V_1 set: the unique non-bonding orbital is antisymmetric with respect to each of the three σ_v mirror planes of the D_{3h} group, and hence must have zero entry on the central vertex of
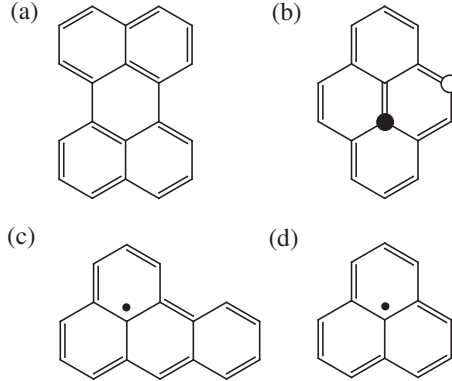
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FIG. 5. Smallest perifused benzenoids of each conduction type identified in the search. They are: (a) perylene (CII); (b) pyrene (XII); (c) benzophenalene (IXX), (d) phenalene (XXX). The two marked vertices in pyrene are a conducting *inter* pair; apart from symmetry images of this pair, all *inter* pairs are insulating.

the molecular graph; as there are no other non-bonding orbitals, this zero entry cannot be compensated by a mirror-symmetric partner orbital, as it would be in similar cases for $\eta > 1$. In spite of the difficulties of conventional synthesis,[6,55,56] the triangulenes are of great interest as possible examples of giant organic molecular magnets and for applications in quantum electronic devices.[6,57,58] In a recent development, individual molecules of triangulene itself $(a = 3)$ have been assembled on Xe, NaCl and Cu surfaces.[59]

X. CONCLUSION

The SSP model allows a complete classification of conduction devices based on bipartite and non-bipartite graphs.

A general scheme for distinct-*ipso*-strong omni-conduction of devices based on bipartite or non-bipartite graphs has been constructed. All types except strong omni-insulators have some chemical representatives.

For bipartite graphs, the available types in the general scheme are fewer, but can be classified more finely. The result is: for devices based on a bipartite graph G with $n \geq 4$ vertices and nullity η, the possible *inter-intra-ipso* omni-conduction types are: $(\eta = 0)$ CII, XII; $(\eta = 1)$ IXX, XXX; $(\eta > 1)$ ICC, IIC, IIX, IXC, IXX, XIX, XXX.

The three connected bipartite graphs with $n < 4$ each uniquely realise a conduction type:

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XXC is possible only for K_1 (isolated vertex); CXI only for K_2 (ethene); ICX only for P_3 (allyl).

Of the nine types possible for $n \geq 4$, two appear to be sparsely represented amongst chemical graphs: so far, only one chemical graph has been found for IIC (non-planar $K_{3,3}$), and no chemical graph for XIX.

For the most important set of bipartite chemical graphs, the benzenoids, the SSP model gives an even simpler conclusion: all catafused benzenoids belong to type CII (they conduct for *all* distinct *inter* pairs of vertices, and otherwise insulate) and perifused Kekulean benzenoids are either CII or XII (they conduct for *some* distinct *inter* pairs). Benzenoids with nullity one also fit into two conduction types, IXX and XXX.

Finally it should be noted that the classification of conduction types, both as here for bipartite graphs and as previously for general graphs, is carried out within an 'empty-molecule' description, in that the incoming ballistic electron does not interact with the electrons already in the molecule. A framework for investigating the effects of Pauli exclusion on conduction is under development,[47] and will allow checks on the robustness of the existing classification of conduction types for both general and bipartite graphs.

Appendix A: Theorems for case-by-case proofs

We list some simple theorems that are useful in eliminating cases from the grand list of 81 TLA. In what follows, η is the nullity of the graph G ($\eta \equiv g_s$). We note that for a bipartite graph, all vertices are either core (CV), in which case deletion lowers η by 1, or core-forbidden (CFV) and *upper*, in which case deletion raises η by 1. ; i.e. a bipartite graph has no *middle* vertices (for which deletion would leave nullity unchanged). As mentioned in the main text, X is interpreted as 'neither C nor I', i.e. a class that is neither fully conducting nor fully insulating, or is empty. The two disjoint vertex subsets of a bipartite graph are V_1 and V_2, with $|V_1| \geq |V_2|$, and the adjacency matrix may be written in block form (with the vertex sets ordered (V_1, V_2)) as

$$\mathbf{A} = \begin{pmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B^t} & \mathbf{0} \end{pmatrix}.$$

1.   Non-singular molecular graphs ($\eta = 0$)

Theorem 0:1 *For a bipartite graph G with $\eta = 0$, the ipso entry of the TLA is I.*

Proof: No vertices of G are CV, so all are CFV upper, and all *ipso* devices insulate (Rule I1). ∎

Theorem 0:2 *For a bipartite graph G with $\eta = 0$ either the intra entry of the TLA is I or the class of intra pairs is empty (and then $G = K_2$, with intra entry X).*

Proof: For $\eta = 0$, $|V_1| = |V_2| = n/2$. Let $\overline{L}$ be in V_2. Then $G - \overline{L}$ has $\eta = 1$ and since deletion of all V_2 vertices gives $\eta = n/2$, $G - \overline{L} - \overline{R}$ (with $\overline{L}$ and $\overline{R}$ in V_2 of G) must have $\eta = 2$. Therefore there is no conduction for *intra* pairs (Rule D1): either the *intra* entry in the TLA is I or there are no *intra* pairs. The only graph with $n > 1$ vertices but no *intra* pairs is K_2, consisting of two vertices joined by a single edge. ∎

Applications of Theorems 0:1 and 0:2 leaves only the TLA III undecided for $\eta = 0$. This case is settled by:

Theorem 0:3 *There are no strong omni-insulators with $\eta = 0$.*

Proof: For a device with $\eta = 0$, a distinct $\overline{L}$, $\overline{R}$ is conducting if and only if the entry in the inverse, $(\mathbf{A}^{-1})_{\overline{L},\overline{R}}$ is non-zero[45]. For a distinct omni-insulator G, $\mathbf{A}^{-1}$ is a diagonal matrix, hence $\mathbf{A}$ is also a diagonal matrix, implying that G is not connected. As distinct omni-insulators with $\eta = 0$ are impossible, then strong omni-insulators with $\eta = 0$ are also impossible. (In fact, strong omni-insulators with $\eta \neq 0$ are also impossible.[45]) ∎

2.   Singular molecular graphs with $\eta = 1$

Theorem 1:1 *For a bipartite graph G with $n > 1$ and $\eta = 1$, the ipso entry of the TLA is X.*

Proof: As G has some CV, some cases of *ipso* conduction occur by Rule I3. Assume that G has $n > 1$ vertices: since G is bipartite it is not a nut graph and hence has some CFV, which give *ipso* insulation by Rule I1. (N.B. If instead G has $n = 1$, the *ipso* entry is C and the whole TLA is XXC as both sets of distinct pairs are empty.) ∎

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Theorem 1:2 *For a bipartite graph G with $\eta = 1$ the intra entry of the TLA is not I.*

Proof: For a bipartite graph with $\eta = 1$, all CV are in the larger subset of vertices, V_1 (the unique NBO is concentrated on the starred vertices of the molecular graph[60]). As G is connected, **A** is not empty but has a zero eigenvalue, so contains at least two CV in V_1. A CV/CV pair is either D9 or D11, but D11 is impossible for $\eta < 2$ and hence the CV pair conducts, by D9. ∎

Theorem 1:3 *For a bipartite graph G with $\eta = 1$, the inter entry of the TLA is not C.*

Proof: At least one CV/CFV *inter* pair exists, as all CV are in V_1, and this is insulating, by D5, so the *inter* entry is I or X. ∎

Application of theorems 1:1 to 1:3 leaves only case XCX undecided. This is settled by:

Theorem 1:4 *For a bipartite graph G with $\eta = 1$, an intra entry of C in the TLA implies entries I for inter and X for ipso.*

Proof: For $\eta = 1$, all CV are in V_1. If the *intra* entry is C then V_1 must consist entirely of CV as a CV/CFV pair would insulate. Then *ipso* is X by I1 and I3 and *inter* is I by D5. ∎

Theorems 1:1 to 1:4 rule out XCX. A singular bipartite graph with $\eta = 1$ belongs to one of three types: ICX, IXX or XXX. Furthermore, the TLA ICX is realised by exactly one graph, which is P_3. To see this, observe that $\eta = 1$ implies $|V_1| - |V_2| = 1$ and since all vertices in V_2 are CFV, we cannot have more than one CFV in V_2 (otherwise it would give an insulating pair by D1). Hence G has one CFV and is a star. The only star with $\eta = 1$ and $n > 1$ is P_3.

3.   Singular molecular graphs with $\eta > 1$

Theorem 2:1 *For a bipartite graph G with $\eta > 1$, the ipso entry of the TLA is not I.*

Proof: Since G has at least one CV, at least one *ipso* device is conducting. ∎

Theorem 2:2 *For a bipartite graph G with $\eta > 1$ if the intra entry in the TLA is C, then the ipso entry is not X.*

Proof: Suppose the *intra* entry is C and the *ipso* entry is X. G must have at least one CFV and at least one CV. If they form an *intra* pair we have insulation by D5 and the *intra* entry

is not C. If there is no CV/CFV *intra* pair, then V_1 is all CV and V_2 is all CFV and the *intra* V_2 pairs are insulating by D1, giving a contradiction. ∎

Theorem 2:3 *For a bipartite graph G with $\eta > 1$, the inter entry is not C.*

Proof: Choose $\overline{L}$ as a CV in V_1. Choose $\overline{R}$ in V_2. Either we have a CV/CFV pair and insulation by D5 or we have a CV/CV pair. In that case, $\overline{R}$ remains a core vertex in $G - \overline{L}$ and we have $\eta - 2$ for the nullity of $G - \overline{L} - \overline{R}$, hence insulation by D11. To see that $\overline{R}$ is CV in $G - \overline{L}$, observe that the CV in each vector in a basis for the nullspace of G can be concentrated in one or other of V_1 and V_2; removal of $\overline{L}$ in V_1 reduces nullity by 1 but all restricted vectors corresponding to CVs in V_2 remain in the nullspace of $G - \overline{L}$. ∎

Theorem 2:4 *For a bipartite graph G with $\eta > 1$, with ipso entry C in the TLA, the inter entry is I.*

Proof: If the *ipso* entry is C, all vertices are CV by I3. For *inter* pairs, we have either D9 or D11, but by the argument used in the proof of Theorem 2:3, if $\overline{L}$ is in V_1 and $\overline{R}$ is in V_2, then $\overline{R}$ is a CV in $G - \overline{L}$ and we have case D11, and insulation for all *inter* pairs. ∎

Appendix B: Graphs of type IIC

As we have seen, $K_{3,3}$ is a chemical graph of type IIC. The small examples of non-chemical graphs in IIC are also complete bipartite graphs, $K_{p,q}$ with $p \geq 3, q \geq 3$. It is easy to show that all such $K_{p,q}$ are of type IIC. $K_{p,q}$ $(p, q > 0)$ has nullity $p + q - 2$ and consists entirely of core vertices. Deletion of one vertex in $K_{p,q}$ $(p, q \geq 3)$ yields $K_{p-1,q}$ or $K_{p,q-1}$ and deletion of two vertices gives $K_{p-2,q}$, $K_{p-1,q-1}$ or $K_{p,q-2}$. These combinations correspond to Rule D11 $(g_s, g_s - 1, g_s - 1, g_s - 2)$, and hence insulation. The only chemical graph of type $K_{p,q}$ $(p, q \geq 3)$ is $K_{3,3}$. Molecular realisation of this graph seems unlikely.

However, the graphs $K_{p,q}$ do not exhaust the type IIC. A family of IIC graphs can be constructed by using the adjacency matrix of a *uniform core graph*, as introduced in Ref. 50. Amongst its other properties, a uniform core graph satisfies Rule D11 for every distinct device. As all vertices are CV, all *ipso* devices based on uniform core graphs satisfy Rule I3. A bipartite graph G can be constructed from *any* uniform core graph H, with adjacency

matrix

$$\mathbf{A}(G) = \begin{pmatrix} \mathbf{0} & \mathbf{A}(H) \\ \mathbf{A}(H) & \mathbf{0} \end{pmatrix},$$

where $\mathbf{A}(H)$ is the adjacency matrix of H. One construction that yields a uniform core graph[50] gives $\mathbf{A}(H)$ as

$$\mathbf{A}(H) = \begin{pmatrix} \mathbf{A}(N) & \mathbf{A}(N) \\ \mathbf{A}(N) & \mathbf{A}(N) \end{pmatrix},$$

where $\mathbf{A}(N)$ is the adjacency matrix of a nut graph, N.

The graph H constructed in this way has N as a subgraph, and therefore is not bipartite.[51] The construction doubles the vertex degrees of the starting nut graph (which were all greater than 1^{51}) and so cannot generate a chemical graph. When a vertex is deleted from G the subgraph obtained remains a core graph. The graphs G are therefore examples of IIC bipartite graphs that are neither chemical graphs nor complete bipartite.

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