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Molecular graphs and molecular conduction: the d-omni-conductors†

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Ernzerhof's source-and-sink-potential (SSP) model for ballistic conduction in conjugated π systems predicts transmission of electrons through a two-wire device in terms of characteristic polynomials of the molecular graph and subgraphs based on the pattern of connections. We present here a complete classification of conduction properties of all molecular graphs within the SSP model. An *omni-conductor/omni-insulator* is a molecular graph that conducts/insulates at the Fermi level (zero of energy) for *all* connection patterns. In the new scheme, we define *d-omni-conduction/insulation* in terms of Fermi-level conduction/insulation for all devices with graph distance d between connections. This gives a natural generalisation to all graphs of the concept of *near*-omni-conduction/insulation previously defined for bipartite graphs only. Every molecular graph can be assigned to a nullity class and a compact code defining conduction behaviour; each graph has 0, 1, $>$1 zero eigenvalues (non-bonding molecular orbitals), and three letters drawn from $\{\mathrm{C},\mathrm{I},\mathrm{X}\}$ indicate conducting, insulating or mixed behaviour within the sets of devices with connection vertices at odd, even and zero distances d. Examples of graphs (in 28 cases chemical) are given for 35 of the 81 possible combinations of nullity and letter codes, and proofs of non-existence are given for 42 others, leaving only four cases open.

1 Introduction

The SSP (source-and-sink-potential) model was introduced by Ernzerhof *et al.*[1–14] as a simple but effective description of ballistic molecular conduction. In its graph theoretical (Hückel) incarnation,[15–25] it predicts transmission as a function of energy for a two-wire device from an expression involving a functional of four characteristic polynomials: those of the molecular graph and three subgraphs. In the context of π systems, a chemical (molecular) graph is one that is connected and has a maximum degree of 3 or less. All-carbon frameworks, as treated here, are represented by unweighted graphs. The graph theoretical formulation of SSP leads to 'selection rules' for conduction at the Fermi level, couched in terms of *nullities*, η, of the molecular graph and the subgraphs (i.e. the numbers of non-bonding π orbitals of the corresponding molecules).[21,26]

Response of the molecular *device* is thereby specified by the underlying molecule and the pattern of connection to the leads. Devices are *distinct*, with leads connected to a pair of graph vertices, or *ipso*, with both leads connected to a single vertex. For unweighted graphs, the theory takes on a particularly simple form. Properties of molecules that contain conjugated heteroatoms can be considered by perturbation methods, as in classic approaches to difficult problems such as the electronic spectrum of porphyrins, where useful results already emerge from treatment as a carbon framework with modified electron count.[27]

A natural question relates to *omni-conduction* and *omni-insulation*: are there molecular graphs that are predicted in the SSP picture to conduct or insulate at the Fermi level consistently for *all* connection patterns? These graphs would be respectively omni-conductors or omni-insulators.[22] Various types of omni-behaviour can be defined in terms of consistent behaviour for *distinct*, *ipso* or *all* devices: these lead to the definition of *distinct*, *ipso* and *strong* omni-conductors/insulators. Nullity again plays a key role.[22]

This variety of behaviour can be captured with a simple classification system. Division into nullity classes 0, 1, and $>$1, combined with conduction (C), insulation (I) or mixed (X) behaviour for distinct and ipso devices leads to a classification of molecular devices into at most 27 categories, each labelled by a *two-letter acronym* and nullity class. The 27 categories reduce to exactly 13 that are realisable by graphs.[25]

There are families of chemical graphs for which omni-

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† *Electronic supplementary information (ESI) available: tabular information on classification of d-omni conduction behaviour of general graphs, and long codes for chemical graphs. See DOI: xxxxxxxxxx*

conducting behaviour is not possible. For them we can define the notion of a *near-omni* conductor, by making a well defined partition of the set of devices arising from a molecular graph. An important class of conjugated systems, including polyenes and benzenoids, consists of the *alternant* hydrocarbons. For these molecules, the molecular graph is *bipartite*. The vertices of a bipartite graph separate into two sets, assigned different colours, such that no edges join vertices of the same colour. The colours correspond to the starred and unstarred atoms of the alternant hydrocarbon.[28] Bipartite molecular graphs cannot have full omni-conduction, for well understood mathematical reasons, but we can make a near-omni[25] classification by separating distinct devices into inter and intra types: in an *intra* device the two connection vertices belong to the same partite set; in an *inter* device they belong to different partite sets. For *ipso* devices, we can ignore the colour of the connection vertex. The nullity class ($\eta = 0$, 1 and > 2) is again important. Bipartite graphs therefore allow a *three-letter* acronym (TLA) for each nullity class. Therefore, in the three-letter formulation, devices are characterised by their *intra*, *inter* and *ipso* behaviour, further distinguished by nullity. It can be proved that the 81 conceivable classes reduce to exactly 14.[25] This treatment suggests a generalisation for near-omni *non-bipartite* graphs.

The central idea used in this generalisation is to partition conduction, insulation and mixed behaviour of a non-bipartite graph according to *graph-theoretical distance*, d, between the connection vertices. This leads to the definition of *d-omni-conductors* and insulators, and a new interpretation of the three-letter acronyms[25] such that they will apply to *all* graphs, whether bipartite or not, and hence cover all possible conjugated hydrocarbons.

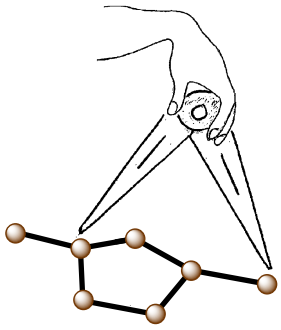

Fig. 1 Schematic of the d-conductor. Here, a pair of connection vertices at fixed distance d = 3 is chosen for attachment to wires in a set of devices.

Specifically, we imagine incorporation of a molecular graph in a circuit through connections chosen via a pair of calipers with a fixed-jaw opening (see Figure 1). For simplicity, we suppose that the calipers span a fixed *graph-theoretical* distance: the calipers touch contacts separated by a fixed distance d (d is the length in edges of a shortest path between connection vertices $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ in the molecular graph, G) drawn from the set $\{d\} = \{0, 1, \ldots, D\}$, where D is the *diameter* of the graph.[29]

We can ask the omni-conduction/insulation question for each d, leading to a $(D + 1)$-dimensional code for each graph. Reduction to three categories (odd-d, (non-zero) even-d, and zero-d) then gives a three-letter short code, which is applicable to all graphs. This classification by distance maps neatly onto the *inter* (odd d), *intra* (even $d \neq 0$) and *ipso* ($d = 0$) cases for bipartite graphs. (All edges of a bipartite graph connect vertices of different colour, and a bipartite graph can contain no odd cycles, so distances between vertices of the same (resp. opposite) colours are all even (odd). Hence, inter $\equiv$ odd-d, intra $\equiv$ even-d, ipso $\equiv$ zero-d, and every bipartite graph keeps the same label as before.) The three-letter classification again gives a maximum of 81 hypothetical cases when C, I, X are combined with nullity classes η = 0, 1, >1.

In the present paper, we explore the possibilities for d-omni and near-d-omni conductors and insulators, show that the 81 cases reduce to a significantly smaller number, and discuss systematics for long and short codes in various families of bipartite and non-bipartite graphs of interest in chemistry. Hence, we will arrive at a compact, universal scheme for classification of Fermi-level conduction within the graph theoretical SSP approach.

2 Background

2.1 The Hückel hamiltonian

The Hückel hamiltonian of an n-centre π-conjugated system can be written

$$\mathbf{H} = \alpha\mathbf{1} + \beta\mathbf{A}, \tag{1}$$

where α and β are the Hückel Coulomb and resonance integrals, $\mathbf{1}$ is the $n \times n$ identity matrix, and $\mathbf{A}$ is the adjacency matrix of the molecular graph, with $\mathrm{A}_{rs} = 1$ for edges, and $\mathrm{A}_{rs} = 0$ otherwise. The eigenvectors of $\mathbf{H}$ correspond to molecular orbitals, and the eigenvalues $\{\lambda_\mathrm{i}\}$ to orbital energies, through $\epsilon_\mathrm{i} = \alpha + \lambda_\mathrm{i}\beta$. Energies are specified with respect to an origin at α and in units of $|\beta|$.

2.2 The SSP model

In the graph-theoretical version of the SSP approach,[15] a device is represented as a molecular graph G attached by internal vertices (atoms) $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ to *source* (L) and *sink* (R) vertices that represent the effect of two semi-infinite wires, which respectively deliver and remove a fraction T of an electron in steady-state ballistic conduction. The transmission T is a function of electron energy, E. The $(n + 2)$-vertex *device* incorporating molecular and distinct source and sink vertices is illustrated in Figure 2.

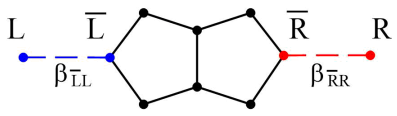

Fig. 2 An SSP molecular device. The molecule is a conjugated π system. Its molecular graph G has n vertices, of which $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ are connected to semi-infinite leads. ($\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ coincide in the *ipso* device.) Each lead is replaced by an extra vertex: source (L) or sink (R), respectively. The whole device is modelled by the $(n + 2)$-vertex graph, with complex weights on source and sink, and real weights (Hückel Coulomb and resonance integrals, α and β) on internal vertices and edges. In this specific example, the molecule is a pentalene framework, with non-bipartite molecular graph G, and 'para' connections via opposite apices of the five-membered rings.

In the SSP treatment, the equation to be solved for transmission is an $(n+2)\times(n+2)$ extension of the eigenvalue equation for the molecular π system, where complex source and sink potentials[1] on the diagonal of the modified adjacency matrix create an electron current consistent with the elastic boundary conditions. Solution of the resulting inhomogeneous equation at each energy E provides a *device wavefunction* from which the transmission factor and all bond currents can be calculated.[1,15,23] Explicit examples of the matrices involved are given for small molecules in, for example, Refs. 5,6.

It turns out that $T(E)$ depends on E through s, t, u and v, the characteristic polynomials of the four graphs G, $G-\overline{\mathrm{L}}$, $G-\overline{\mathrm{R}}$ and $G-\overline{\mathrm{L}}-\overline{\mathrm{R}}$. At $E=0$ (the Fermi energy) the transmission is given by the limit of a ratio of high-order polynomials:[22]

$$T(0)=\lim_{E\to 0}\frac{4j^2\tilde{\beta}^2}{\left[(s-v\tilde{\beta}^2)^2+(u+t)^2\tilde{\beta}^2\right]}. \qquad (2)$$

where j^2 is the determinantal combination $ut-sv$ and $\tilde{\beta}$ is a device parameter determined by relative magnitudes of resonance integrals for intra-wire, wire-to-molecule, and intra-molecule contacts.[17] The transmission spectrum, the curve of T as a function of E, typically varies rapidly and repeatedly within its allowed range of zero to one. These oscillatory features tend to be smoothed out in the current-voltage device response curve. Selection rules for transmission are independent of the precise values of the parameters that go to make up $\tilde{\beta}$.

2.3 Selection rules

Selection rules[21,26] for Fermi-level conduction of the devices $\{G,\overline{\mathrm{L}},\overline{\mathrm{R}}\}$ follow from Eq. (2) by considering the nullities of the graphs G, $G-\overline{\mathrm{L}}$, $G-\overline{\mathrm{R}}$ and $G-\overline{\mathrm{L}}-\overline{\mathrm{R}}$, or equivalently the numbers of zero roots of the characteristic polynomials s, t, u and v. The Cauchy Interlacing Theorem[30] leads to a small set of possibilities, as listed in Table 1, predicting Fermi-level conduction or insulation of a device according to 11 distinct and 3 ipso cases.

2.4 Vertex types

The Interlacing Theorem allows partition of the vertices of the molecular graph into three types: *lower*, or *core* vertices (CV) and core-forbidden vertices (CFV) of types *middle* and *upper*.[22,31,32] Deletion of a CV lowers nullity by 1, deletion of a middle CFV leaves it unchanged, and deletion of an upper CFV increases the nullity by 1. Bipartite graphs cannot have middle vertices, as n and η necessarily have the same parity for these graphs.

The CV/CFV terminology comes about because the vertices that lower the nullity on deletion are exactly those that have a non-zero entry in some vector in the graph nullspace, i.e. are 'within the core' of the graph. In chemical terms, core vertices are those with a non-zero contribution to the charge/spin density resulting from half/full occupation of the set of non-bonding orbitals in the π system. Conversely, a core-forbidden vertex makes zero contribution in these cases.

One simple consequence of the definitions is that if a vertex has one CV neighbour, then it must have at least two, as the neighbourhood of every vertex i in a non-bonding vector obeys a zero-sum rule for entries on the neighbours j of i.

Furthermore, one useful observation is that the distance between a pair of CV that are neighbours of a middle CFV is not always 2; it might be 1 if G contains triangles. This awkward fact complicates construction of proofs.

Table 1 Selection rules for Fermi-level conduction of molecular devices based on graphs with nullity $\eta_s=\eta$. Each signature $\{\eta_t,\eta_u,\eta_v,\eta_j\}$ for nullities of the subgraphs and zero roots of the combination $|j|=\sqrt{ut-sv}$ leads to a prediction of $T(0)\neq 0$ (conduction), or $T(0)=0$ (insulation). Devices are labelled D for *distinct* and I for *ipso*

Rule	η_s	η_t	η_u	η_v	η_j	$T(0)$
D1	η	$\eta{+}1$	$\eta{+}1$	$\eta{+}2$	$\geq\eta{+}1$	$=0$
D2	η	$\eta{+}1$	$\eta{+}1$	η	η	$\neq 0$
D3	η	$\eta{+}1$	η	$\eta{+}1$	$\geq\eta{+}1$	$=0$
D4	η	$\eta{+}1$	η	η	η	$\neq 0$
D5	η	$\eta{+}1$	$\eta{-}1$	η	$\geq\eta$	$=0$
D6	η	η	η	$\eta{+}1$	η	$\neq 0$
D7.1	η	η	η	η	η	$\neq 0$
D7.2	η	η	η	η	$\geq\eta{+}1$	$=0$
D8	η	η	$\eta{-}1$	$\eta{-}1$	$\geq\eta$	$=0$
D9	η	$\eta{-}1$	$\eta{-}1$	η	$\eta{-}1$	$\neq 0$
D10	η	$\eta{-}1$	$\eta{-}1$	$\eta{-}1$	$\eta{-}1$	$\neq 0$
D11	η	$\eta{-}1$	$\eta{-}1$	$\eta{-}2$	$\geq\eta{-}1$	$=0$
I1	η	$\eta{+}1$				$=0$
I2	η	η				$\neq 0$
I3	η	$\eta{-}1$				$\neq 0$

2.5 Calculations

Spectral representations and Laurent expansions allow calculation of all the various required nullities needed for the selection rules directly from the eigenvectors and eigenvalues of the adjacency matrix of G alone,[22,25] with assignment of cases D1 to I3 and prediction of conduction or insulation, device by device. This gives an algorithm for detection of conduction behaviour across the whole family of devices based on a particular graph. This toolkit was earlier used to find two- and three-letter acronyms, and is employed again here to obtain the three-letter d-omni classification.

3 Classification of conduction behaviour

We discuss three levels of classification: the two-letter code, specialisation to a three-letter code for bipartite graphs, and generalisation of this code to cover all graphs.

3.1 Two-letter codes (all graphs)

We classify devices based on a given graph G (chemical or otherwise) as either distinct or ipso. For each class of devices we assign a letter {C, I, X} to denote respectively the cases where all devices conduct at the Fermi level, all insulate, or the class has mixed behaviour (or is empty). We further label the classes of devices by nullity of G with $\eta=0$, $\eta=1$ and $\eta>1$.

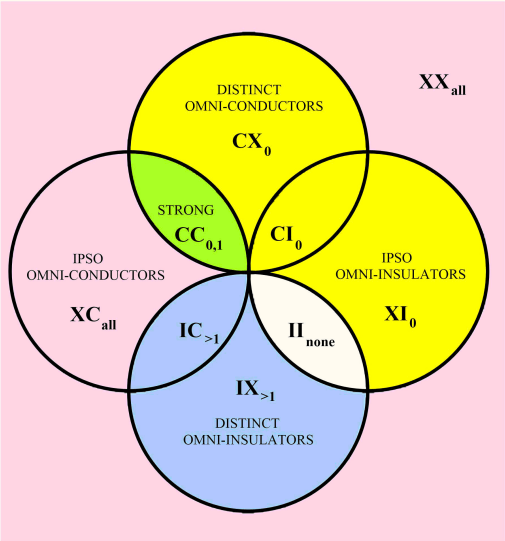

Fig. 3 Venn-like diagram showing the two-letter (distinct/omni) classification of conduction behaviour in the SSP model of all possible molecular graphs where C, I and X stand for conduction, insulation and mixed, and subscripts denote the nullity classes (0, 0 and 1, $>$1, all or none) for which the two-letter code applies.

Of the 27 class labels consisting of two letters and a nullity, it can be proved[25] that 13 correspond to realisable devices $\{G, \overline{\mathrm{L}}, \overline{\mathrm{R}}\}$ and the others label empty classes (impossible devices). A special case is II, which is not realisable for any nullity.[22] Figure 3 shows the realisable combinations of two letters and nullity. Another way of representing these data is through eight realisable two-letter pairs, with four sets of nullity restrictions. This is illustrated by the shading scheme in the on-line colour version of the figure, where each colour is common to regions of the diagram that have the same combination of nullity classes.

Table 2 Expansion of two-letter to three-letter acronyms. Each combination is labelled with allowed nullity values.[25] Note that II $\rightarrow$ III is an impossible combination.[22] Not all TLA compatible with a given 2LA exist.

Nullity	2LA	TLA
0, 1	CC	CCC
0	CI	CCI
0	CX	CCX
>1	IC	IIC
none	II	III
>1	IX	IIX
0, 1, >1	XC	CIC, CXC, ICC, IXC, XCC, XIC, XXC
0	XI	CII, CXI, ICI, IXI, XCI, XII, XXI
0, 1, >1	XX	CIX, CXX, ICX, IXX, XCX, XIX, XXX

3.2 Three-letter codes (bipartite graphs)

At the next level of classification we treat only bipartite graphs, and partition the distinct devices into inter and intra, according to whether connections $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ belong to different or identical partite sets. Again, we use an alphabet of three letters {C, I, X} for omni-conducting, omni-insulating, and mixed or non-existent sets. The nine two-letter combinations split into 27 three-letter combinations, as shown in Table 2. This table already shows that there are some disallowed combinations of letter code and nullity.

If G is bipartite, it can be proved[25] that only 14 out of the 27 $\times$ 3 combinations of letters and nullities are possible. The allowed classes of bipartite devices having *inter-intra-ipso* conduction types of the three kinds, for graphs with $n \geq 4$ vertices and nullity η are:

$$\begin{aligned} \eta = 0 \quad & \mathrm{CII}, \mathrm{XII}; \\ \eta = 1 \quad & \mathrm{IXX}, \mathrm{XXX}; \\ \eta > 1 \quad & \mathrm{ICC}, \mathrm{IIC}, \mathrm{IIX}, \mathrm{IXC}, \mathrm{IXX}, \mathrm{XIX}, \mathrm{XXX}. \end{aligned}$$

The three connected bipartite graphs with $n < 4$ each uniquely realise a conduction type: K_1 (isolated vertex) is apparently the only bipartite graph of type XXC, though other non-bipartite examples exist (see below); CXI appears for K_2 (ethene), and ICX for P_3 (allyl).

3.3 Three-letter codes (all graphs)

What happens if we use an alternative subdivision of distinct devices? Distinct devices have $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ at non-zero graph theoretical distance, d. We can make a subdivision into distinct devices with odd-d, and even-d, respectively. (For brevity, we can call these *odd* and *even* devices, respectively.) For bipartite graphs G, the odd/even dichotomy maps exactly onto the inter, intra subdivision, so bipartite graphs retain their old codes, but now non-bipartite graphs G can also be included in a common scheme. We now investigate how many of the 27 $\times$ 3 = 81 combinations of three letters and nullity type are possible for chemical graphs (connected graphs with maximum degree at most three) and general graphs (connected graphs with no limitation on degree), whether bipartite or non-bipartite.

As in previous work we adopt a two-pronged approach. First, we check large sets of examples to find which classes (combinations of a three-letter acronym and nullity type) have examples amongst small graphs. Then we attempt to prove the emptiness of the remaining classes.

Assignment of conduction behaviour was carried out by taking sets of graphs from various graph generators, and using the previously developed[22] conduction/insulation decision-tree filters based on the selection rules. Numerical eigenvectors of the adjacency matrix of G are used to compute coefficients in Laurent expansions of scaled structural polynomials $\hat{t} = t/s$, $\hat{u} = u/s$, $\hat{v} = v/s$ and $\hat{\jmath} = \jmath/s$, and use them with the filters to assign conduction or insulation.

The datasets of graphs were generated with *nauty*[33] (general and chemical graphs), *plantri*[34] (cubic polyhedra), *fullgen*[35] and *CaGe*[36] (for fullerenes and benzenoids). We also searched databases of larger vertex-transitive and two-orbit graphs, provided by Gordon Royle.[37] All graphs considered here are simple (with no loops or multiple edges) and connected.

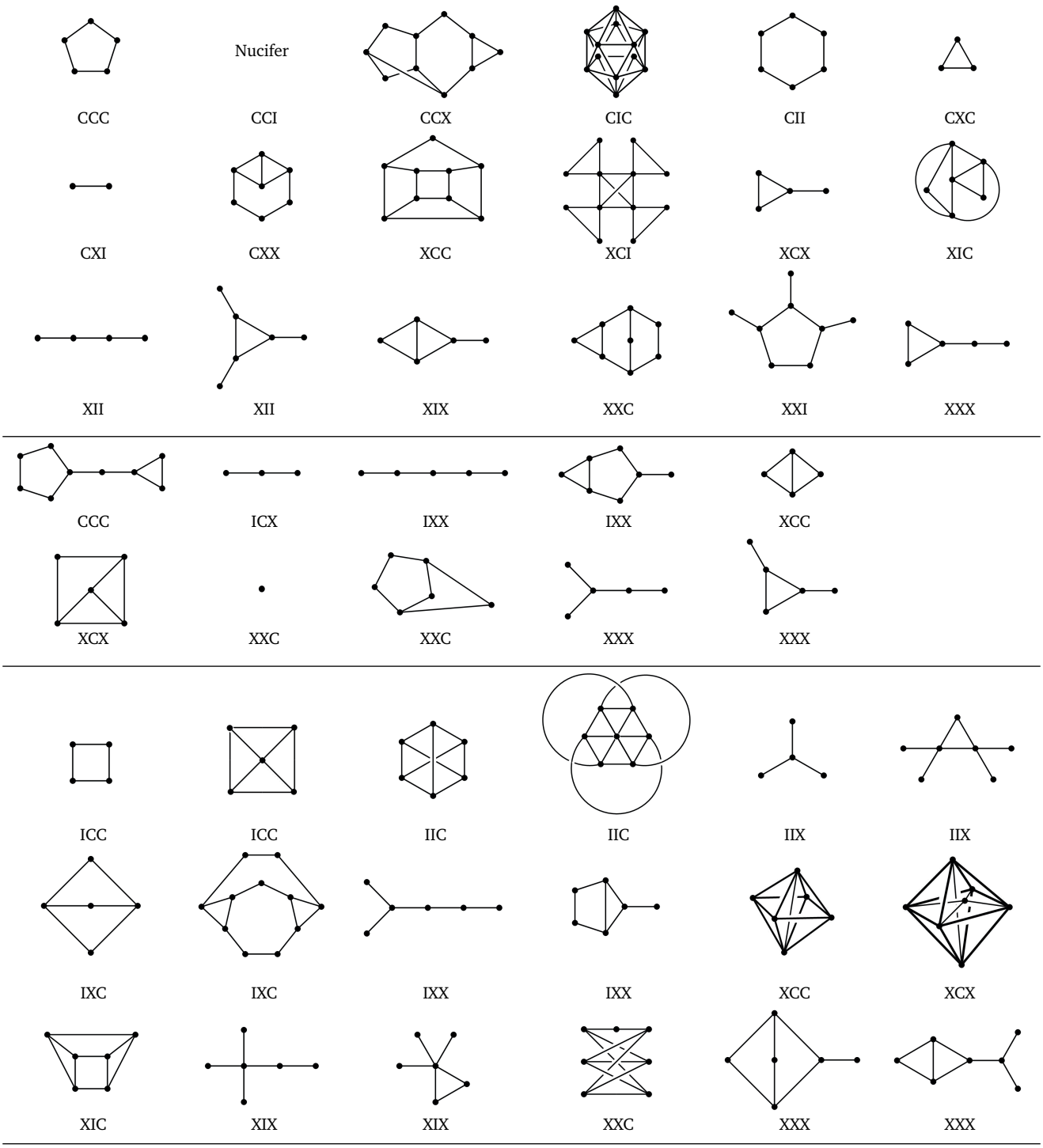

Fig. 4 Realisation of d-omni-conduction types classified by three-letter acronym and nullity. The top panel shows the cases for $\eta = 0$, and the entry 'Nucifer' is a placeholder for the smallest example of class CCI. The graph for category CIC is the skeleton of the icosahedron. The middle panel shows $\eta = 1$. The bottom panel shows $\eta > 1$, and case IIC is the 'utilities graph', $K_{3,3}$, which appears to be the only chemical graph in this class. In each case, a chemical example is given,if we have one, and bipartite and non-bipartite examples are given where we have both.

Table 3 Distribution over allowed classes for two-letter codes of chemical graphs on $n \leq 14$ vertices

Case	η	Vertex count													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
CC	0			1	1	1	2	5	8	13	48	77	333	858	3721
CI	0		1												
CX	0										5		9		151
XC	0							1	4	11	25	108	270	1178	3553
XI	0				1		6		24		132		902		7669
XX	0				1	2	7	17	71	177	707	1904	8762	25469	126365
CC	1									1		8	9	27	23
XC	1	1			1		2		10	7	42	54	285	539	2773
XX	1			1		6	3	35	27	261	322	2660	3963	32252	55733
IC	>1						1								
IX	>1				1			1		1	2	2	3	6	10
XC	>1				1	1	1	1	1	8	21	48	110	317	729
XX	>1						6	4	49	52	429	663	4784	8676	61317
Total count		1	1	2	6	10	29	64	194	531	1733	5524	19430	69322	262044

Table 4 Distribution over allowed classes for three-letter codes of bipartite chemical graphs on $n \leq 14$ vertices

Case	η	Vertex count													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
CII	0						1		2		4		11		47
CXI	0		1												
XII	0				1		4		18		96		605		4691
ICX	1			1											
IXX	1					1		4		12		62		366	
XXC	1	1													
XXX	1					2		10		61		413		3311	
ICC	>1				1				1				2		2
IIC	>1						1								
IIX	>1				1			1		1	2	2	3	6	10
IXC	>1					1				1	3	3	5	5	13
IXX	>1						4	3	17	21	85	141	530	1014	3904
XXX	>1						2		14	5	105	80	918	934	8585
Total count		1	1	1	3	4	12	18	52	101	295	701	2074	5636	17252

Table 5 Distribution over allowed classes for three-letter codes of chemical graphs on $n \leq 14$ vertices

Case	η	Vertex count													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
CCC	0					1	2	5	8	13	48	77	333	858	3721
CCX	0										5		9		151
CII	0						1		2		4		11		47
CXC	0			1	1			1		2	1	11	9	65	87
CXI	0		1												
CXX	0							1	1	6		7	33	49	157
XCC	0									3	4	29	20	214	205
XCX	0				1				1		8	18	14	59	291
XII	0				1		5		19		105		658		5079
XIX	0					1		1	1	5	1	23	5	153	21
XXC	0								4	6	20	68	241	899	3261
XXI	0								3		23		233		2543
XXX	0					1	7	15	68	166	698	1856	8710	25208	125896
CCC	1									1		8	9	27	23
ICX	1			1											
IXX	1					1		5		18		93		552	
XCC	1				1						1				2
XCX	1					1				1				1	
XXC	1	1					2		10	7	41	54	285	539	2771
XXX	1					4	3	30	27	242	322	2567	3963	31699	55733
ICC	>1				1				1				2		2
IIC	>1						1								
IIX	>1				1			1		1	2	2	3	6	10
IXC	>1					1				1	3	4	6	6	15
IXX	>1						5	3	22	26	118	200	807	1643	6709
XIC	>1						1						7		
XXC	>1							1		7	18	44	95	311	712
XXX	>1						2	1	27	26	311	463	3977	7033	54608
Total count		1	1	2	6	10	29	64	194	531	1733	5524	19430	69322	262044

4 Results

4.1 Allowed d-omni codes

A search of chemical graphs with vertex counts $n \leq 14$, general graphs with $n \leq 11$, and vertex-transitive and two-orbit graphs with $n \leq 24$ already supplies examples of 35 of the 81 conceivable combinations of TLA and nullity class.

Tables 3, 4 and 5, show statistics derived from these searches on occurrence of two and three-letter codes for chemical graphs. Equivalent statistics for general graphs are collected in tables in the ESI.†

Throughout the tables, cases not listed are provably forbidden, have smallest examples outside the range of n (CCI, $\eta = 0$, CIC $\eta = 0$, IXC $\eta > 1$), or are unresolved (CIC $\eta = 0$, ICC $\eta = 1$, IXC $\eta = 1$, ICX $\eta > 1$). An exhaustive search of all 1,006,700,565 general graphs on 11 vertices adds only IXC $\eta > 1$ to the list of found cases obtained for $n \leq 10$.

One interesting case is that of the *nuciferous graphs* (or *nucifers*), which are non-singular graphs (i.e. with $\eta = 0$) that are conducting for all distinct devices but insulating for all ipso devices, i.e. with code CCI for graphs where inter, intra and ipso classes of device are all non-empty. K_2 is the trivial nucifer with no intra devices, and unique TLA CXI. All non-trivial nucifers are non-chemical;[38] vertex-transitive examples are known with $n \geq 24$,[39] and in the present work we were able to find smaller examples, with $n \geq 18$, by considering graphs with two orbits of vertices. Hence, the class CCI with $\eta = 0$ is in fact populated, though not by chemical graphs. Fig. 4 shows small examples for the 35 cases (chemical where we have one, and bipartite and non-bipartite where we have both).

Next we concentrate on eliminating impossible combinations. Limitations imposed by the unrealisable subset of two-letter/nullity codes[22] can be used to rule out some three-letter/nullity codes. This removes 25 of the 81 cases.

A further simple argument about non-zero entries in the inverse adjacency matrix removes all codes of type I** with $\eta = 0$, hence eliminating a further six cases.

Appendix A lists these and other theorems that can be used to prune the possibilities still further. Table 6 shows the state of play, where 35 classes have examples and 42 are provably empty. At present, we have 4 stubborn classes that are undecided, with neither examples nor a proof that there can be none.

The populations of the various classes for small numbers of vertices vary considerably. Chemical graphs are found in nearly all the mathematically possible classes, though some classes are very sparsely represented. Statistically, XXX is expected to be the most common label. In such cases, the SSP model predicts mixed behaviour across all devices in the odd, even or ipso subclasses that can be derived from the given molecule. The interesting fact is that so many chemical graphs do have specific conduction behaviour. With the near-omni classification,[25] it was found that all cata-fused benzenoids are covered by one case (CII with $\eta = 0$), and all Kekulean benzenoids by two (CII and XII, $\eta = 0$) . Similarly, with the d-omni classification derived here, most fullerenes translate to CCC.[20]

Incidentally, Table 6 constitutes an alternative proof of the sufficiency of the 13 2-letter codes to describe all graphs. Theorem A.1 rules out 13 cases, and another, CX with $\eta = 1$, is ruled out by theorem A.3 or by the simpler argument that for this nullity, C* implies a nut graph, but a nut graph implies *C.

4.2 Expanded d-omni codes

Useful though the short three-letter acronyms are in labelling families of bipartite and non-bipartite graphs, it could be interesting to explore the more detailed information afforded by the full d-omni approach. We define the *long code* for a molecular graph as a string of (D + 1) letters drawn from the alphabet {C, I, X}, where each letter refers to the conduction behaviour of devices with a fixed value of d, drawn from the range d = 0, 1, ..., D, where D is the diameter of the graph. Notice that the entries in the long code are ordered strictly by increasing d, with alternating even and odd devices starting from ipso $d = 0$. Instead, the TLA has *ipso* at the final position, for consistency with previous usage.[25]

Some long codes are obvious, determined entirely by a three-letter acronym that contains no X in the first two positions. Others show more complex patterns. The final figure and table of the ESI† analyse long codes for a number of graph families.

5 Conclusions

An important advantage of the SSP (Source-and-Sink-Potential) model for ballistic conduction is its essentially graph theoretical nature, which enables qualitative prediction (selection rules) for conduction or insulation at the Fermi level. These allow classification of the whole set of devices associated with different patterns of connection of two wires to a given molecular structure. In previous work, the initial concepts of omni-conduction and omni-insulation[22] have been successively refined to describe systematics of conduction within chemically significant subsets of these devices. A scheme for bipartite graphs was reported earlier.[25] The present paper has presented a new classification based on graph distance, which can deal with the molecular graph of any conjugated π system. Of the 81 hypothetical conduction types, 77 have been resolved: 35 are realised by small graphs; 42 are unrealisable by any graph; 4 are still open. Of the 35 realised cases, at least 28 are exemplified by a chemical graph representative of a conjugated π system. The new scheme is compatible with the previous classification of bipartite graphs but now covers all π systems, alternant and non-alternant.

The classification derived here is complete, in that every possible single-molecule, two-lead device based on a carbon framework has its place within the structure. Benzenoids fit within the near-omni classification already; important non-alternant molecules such as the fullerenes are captured by the new scheme. Binary conduction/insulation classification of single devices already yields useful correlations with experiment for alternant molecules (see Ref. 21 for a real-world application where the rules correctly distinguish between isomeric devices that have conductivities differing by two orders of magnitude[9,40]). The new classification extends this range to the full space of carbon frameworks.

Conflicts of interest

There are no conflicts to declare.

Appendix A Theorems for d-omni codes

The tripartite classification of vertices into lower (core, CV), middle (CVF) and upper (CFV) types will be used repeatedly in this section. Wildcard characters are used to stand for arbitrary letters drawn from the {C, I, X} alphabet. Hence, A*B indicates a code with behaviour A at odd d, B at zero d and C, I or X at even d.

A remark on notation: the dual use of the letter X to signify either the absence of devices in a class or the presence of mixed conduction/insulation for device in a class requires some care when comparing two- and three-letter acronyms. For example, the complete graph K_n for $n > 2$ is a strong omni-conductor. The two-letter acronym for $K_{n>2}$ is CC but the TLA is CXC, as $d \leq 1$ for any complete graph on $n > 1$ vertices, so the class of devices with even distance $d \geq 2$ is empty. For $2 \leq n \leq 6$ the code CXC applies in this sense to complete graphs; from $n \geq 7$ there are also graphs with the same TLA code, but now with the X standing for mixed behaviour for distinct devices with even distance between the connections. The distinction is obvious from the long code, or just from the graph diameter, but it needs to be kept in mind when looking at how two- and three-letter acronyms are correlated.

In deriving rules for exclusion of cases, we begin by noting the combinations that are forbidden by previous results. From the theorems proved in Ref. 22, 25 of the 81 TLA can be ruled out immediately.

Theorem A.1 *The following 25 cases are not realisable by any graph.*

$\eta = 0$ IIC, III, IIX

$\eta = 1$ CCI, CII, CXI, ICI, IIC, III, IIX, IXI, XCI, XII, XXI

$\eta > 1$ CCC, CCI, CCX, CII, CXI, ICI, III, IXI, XCI, XII, XXI

Furthermore, a simple argument based on linear algebra eliminates more classes for $\eta = 0$. The key result is:[22]

Theorem A.2 *For $\eta = 0$, a device with connections $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ is conductive at the Fermi level if and only if the corresponding off-diagonal element in the inverse of the adjacency matrix of the graph is non-zero.*

Proof: For $\eta = 0$, the device with connections $\overline{\mathrm{L}}$ and $\overline{\mathrm{R}}$ conducts if and only if $\jmath_{\overline{\mathrm{L}}\,\overline{\mathrm{R}}} = adj(A)_{\overline{\mathrm{L}}\,\overline{\mathrm{R}}} \neq 0$, and since the determinant of $\mathbf{A}$ is not zero for $\eta = 0$, the device therefore conducts if and only if $(A^{-1})_{\overline{\mathrm{L}}\,\overline{\mathrm{R}}} \neq 0$. ∎

Corollary A.1 TLA I$**$ *is not realisable by any non-singular connected graph.*

Proof: TLA I$**$ implies $(A^{-1})_{ij} = 0$ for all edges i-j ($d = 1$). But then $(AA^{-1})_{ii} = \sum_{j\sim i} A_{ij}(A^{-1})_{ji} = 0$ for all i, in contradiction of the defining property of the inverse that

$$\left(AA^{-1}\right)_{ii} = (A^{-1}A)_{ii} = 1.$$

∎

The corollary adds a further six to the list of unrealisable cases listed in Theorem A.1. An easy consequence of the property used in the proof of Corollary (A.1) is that *every* vertex $\overline{\mathrm{L}}$ of a *non-singular* connected graph G is part of at least one conducting device where $\overline{\mathrm{R}}$ is a neighbour of $\overline{\mathrm{L}}$. There are at least $\lceil n/2 \rceil$ such edgewise-conducting devices. In particular, all leaves u-w in a non-singular graph G define a conducting device (G, u, w).

Another straightforward observation is

Lemma A.1 X *in the ipso position implies that both middle and upper vertices are present (for $\eta = 0$), and at least upper and lower vertices are present (for $\eta \geq 1$).*

This is used to prove:

Theorem A.3 C*X *with $\eta \geq 1$ is not realisable.*

Proof: By Lemma A.1, X in the ipso position implies vertices CV and upper CFV are present in G. Middle CFV vertices may also be present. As the graph is connected it must have at least one edge ($d = 1$) connecting a CV and either an upper or a middle CFV, which are Cases D5 and D8, respectively, and insulating, contradicting the claimed conduction for all devices with odd d.

∎

Theorem A.3 eliminates a further five cases.

Lemma A.2 *All graphs with $\eta \geq 1$ on $n > 2$ vertices have at least two core vertices.*

Proof: For $\eta = 1$, the nullspace contains a unique eigenvector. Either the graph has only core vertices and $|\mathrm{CV}| = n$ and by hypothesis $n > 1$, or there is a core–forbidden vertex v adjacent to a core vertex u and the zero–sum rule for entries in the eigenvector on the neighbourhood of v demands at least one additional neighbour of v to be a core vertex.

For $\eta > 1$, the nullspace contains η independent eigenvectors and a given core vertex u can be assigned a zero entry in at least one vector by taking a linear combination, but again by the zero–sum rule for the neighbourhood of each vertex, this vector must contain at least one non–zero entry, and so $|\mathrm{CV}| \geq 2$.

∎

An alternative proof of Lemma A.2 is the following. For $\eta \geq 1$, CV is not empty and the zero-sum rule for a neighbour of a vertex in CV forces at least two non-zero entries in a kernel eigenvector.

Lemma A.3 *If $\eta \geq 1$ and G has at least one* CFV *(i.e. G is not a core), then there exists an edge* CV-CFV.

Lemma A.4 *If $\eta \geq 1$ then there exist at least two* CV*s, which must have ipso conduction exists, and hence $**$*I *is impossible.*

Lemma A.5 *If $\eta \geq 1$ and the* TLA *code is $**$*C*, then the graph has no upper* CFV *vertices.*

Theorem A.4 CIC *and* CXC *with $\eta = 1$ are not realisable.*

Proof: The TLA code with C in the ipso position means one of two things: either the graph G has only core vertices and it is a nut graph with the TLA code CCC. Or else, G must have core vertices and middle CFV. Since G is connected, there exists an insulating

Table 6 Summary of conduction behaviour of π-conjugated hydrocarbons, showing the existence status of the 81 conceivable combinations of *odd-even-ipso* device behaviour with nullity of the molecular graph. 'Some' indicates that at least one example has been found. An entry 'A:number' refers to the first theorem that can be used to rule out a given case. Cases marked with a star are unresolved

Case	Nullity, η			Case	Nullity, η			Case	Nullity, η		
	0	1	>1		0	1	>1		0	1	>1
CCC	Some	Some	A.1	ICC	A.2	*	Some	XCC	Some	Some	Some
CCI	Some	A.1	A.1	ICI	A.2	A.1	A.1	XCI	Some	A.1	A.1
CCX	Some	A.3	A.1	ICX	A.2	Some	*	XCX	Some	Some	Some
CIC	Some	A.4	A.5	IIC	A.1	A.1	Some	XIC	Some	A.6	Some
CII	Some	A.1	A.1	III	A.1	A.1	A.1	XII	Some	A.1	A.1
CIX	*	A.3	A.3	IIX	A.1	A.1	Some	XIX	Some	A.6	Some
CXC	Some	A.4	A.5	IXC	A.2	*	Some	XXC	Some	Some	Some
CXI	Some	A.1	A.1	IXI	A.2	A.1	A.1	XXI	Some	A.1	A.1
CXX	Some	A.3	A.3	IXX	A.2	Some	Some	XXX	Some	Some	Some

CV-CFV edge (Case 8) contradicting the C in the first position of the TLA codes CIC and CXC.

■

Hence, two further combinations are eliminated.

Theorem A.5 CIC *and* CXC *with* $\eta > 1$ *are not realisable.*

Proof: C in the ipso position implies that G has CV and possibly some middle vertices. However, there can be no CV-middle edge, as this would imply insulation for at least one device with $d = 1$ device, and in the TLA we have C for all odd d. Hence there are no middle vertices, and G is a core.

Consider a CV-CV edge pair u, v. Choose a kernel vector that has non-zero entries at positions u and v. The device $\{G, u, v\}$ is not Case 11, because this would be an insulator, in contradiction of the C entry in the first position of the TLA. Hence, there exists a basis containing $\mathbf{x}$ such that all vectors other than $\mathbf{x}$ in this basis must have zero entries at position u and position v, as otherwise we would have a Case 11 (insulating edge). G is connected, so by induction on edge pairs it is possible to choose a kernel eigenvector with *all* entries non-zero, forcing all other kernel vectors to be filled by zeroes. This is a contradiction of the claim that G has $\eta > 1$.

Note that CCC is already proved impossible for $\eta > 1$ by Theorem A.1, which follows from Theorem 4.3 in a previous paper,[22] so in fact we have that C*C is impossible for $\eta > 1$.

■

Theorem A.6 XIC *and* XIX *with* $\eta = 1$ *are not realisable.*

Proof: Let G be a graph with TLA code XIC or XIX. First note that G is not a nut graph (as the TLA code is not CCC). An entry C or X in the *ipso* position implies that G has at least 2 CVs and at least one middle CFV, because it is an ipso omni-conductor that is not a nut. Therefore, there exist Cases 5 or 8 insulation for a CV–middle CFV pair or a CV–upper CFV pair that are either at odd or even distance apart. XIC and XIX allow both.

All CV–CV pairs give conduction since Case 11 cannot occur (owing to $\eta = 1$). As the TLA implies that all pairs with d even must give insulation, it follows that members of every CV–CV pair are separated by an odd distance.

Possibility 1: All CVs induce a core which is the union of cliques (K_p, $p > 1$). This gives a contradiction since the core has to induce a singular graph. (Note that complete graphs are not singular, for $p > 1$.)

Possibility 2: There exist CVs that form an independent set such that each pair is at distance 3, 5, etc apart. Each middle CFV adjacent to a CV must be adjacent to at least 2 CVs, by the zero–sum rule. Hence, either there exists an edge between the two CVs and so a middle CFV and its two adjacent CVs are on a triangle, or else, there is no edge between the 2 CVs that are adjacent to the middle CFV. In the former case where there is an edge between the 2 CVs, then the CVs are not independent and so give rise to a clique that is non–singular. In the latter case where there is no edge between the 2 CVs, these 2 CVs are an even distance apart and these can only give rise to conduction by Case 9 or 10. Thus, in either of these two cases, a contradiction results for XIC and XIX. ■

The combination of Theorems A.1 and A.6, shows that XI* with $\eta = 1$ is not realisable. Thus, the codes CIX with $\eta = 0$, ICC and IXC with $\eta = 1$ and ICX with $\eta > 1$ are the only codes left either to be proved unrealisable or furnished with an example.

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