Writing with ring currents: selectively hydrogenated polycyclic aromatics as finite models of graphene and graphane

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Alternating partial hydrogenation of the interior region of a polycyclic aromatic hydrocarbon gives a finite model system representing systems on the pathway from graphene to the graphane modification of the graphene sheet. Calculations at the DFT and coupled Hartree–Fock levels confirm that \( sp^2 \) cycles of bare carbon centres isolated by selective hydrogenation retain the essentially planar geometry and electron delocalization of the annulene that they mimic. Delocalization is diagnosed by the presence of ring currents, as detected by ipsocentric calculation and visualization of the current density induced in the \( \pi \) system by a perpendicular external magnetic field. These induced ‘ring’ currents have essentially the same sense, strength and orbital origin as in the free hydrocarbon. Subjected to the important experimental proviso of the need for atomic-scale control of hydrogenation, this finding predicts the possibility of writing single, multiple and concentric diatropic and/or paratropic ring currents on the graphene/graphane sheet. The implication is that pathways for free flow of ballistic current can be modelled in the same way.

1. Introduction

Although much of the avalanche of recent research on graphene and related carbon nanostructures has been concentrated on physical properties [1–3], strategies for chemical functionalization of these materials are receiving increasing attention [4–12]. Controlled
regio-functionalization would offer the intriguing prospect of ‘writing’ circuit diagrams onto the conducting carbon sheet [4] by, for example, selective hydrogenation. Graphane, the fully hydrogenated derivative of graphene, was proposed as a theoretical possibility by Sofo et al. [13], who found a low-energy structure resulting from hydrogenation of both faces of a sheet of carbons that are rings in the chair conformation (figure 1). In this structure, every CH bond is in a favourable antiperiplanar relation to its nearest neighbours, but other combinations of ring conformations in the carbon sheet are also predicted to be competitive in energy for graphane, and some of these may be present in experimental samples [14]. Experimental evidence for graphane comes from the work of Elias et al. [15], who reacted atomic hydrogen with free-standing graphene films. Partial hydrogenation can also be achieved, as in the work of Balog et al. [16], which demonstrated the formation of graphane-like islands on a graphene sheet grown on an Ir(111) substrate. Fluorinated analogues are also accessible. Cheng et al. [17] have synthesized multilayer graphene fluoride and found evidence for a perfluoro-graphane-like structure.

Finite analogues of graphene have, in fact, been known for a long time in chemistry, in the guise of large benzenoids of the polycyclic aromatic hydrocarbon (PAH) family. This analogy is acknowledged in the increasing use of ‘nanographene’ [18] and ‘graphene flake’ [19] as synonyms for older terms such as ‘giant PAH’ [20]. In this picture, benzenoid PAH molecules are regarded as fragments of graphene that have been passivated by termination of dangling bonds with H atoms. This paper suggests an extension of this analogy to structures that would correspond to ‘nanographanes’. Specifically, we consider model systems constructed by full or partial saturation of the two ‘faces’ of a benzenoid (figure 2). A \( \text{C}_n \text{H}_m \) system constructed in this way is not necessarily the lowest-energy form of that hydrocarbon, but, as we will see, it typically occupies a local minimum on the potential energy surface for the finite system and, by extension, remains locally stable when embedded in an infinite analogue. Selective hydrogenation of the nanographene, or dehydrogenation of the nanographane, gives a model for the printing/etching of conduction channels on the graphene/graphane sheet.

For device applications, delocalization of the \( \pi \) -electron distribution and the ability of a system to support flow of \( \pi \) current are key properties. For example, in finite systems, the ring currents induced by external magnetic fields can act as proxies for these properties: ring current maps have been shown to correlate well with cyclic delocalization indices for PAHs [21], and the paths taken by ring currents and by electrons driven by a potential difference through an aromatic system [22] show clear similarities. A primary question for applicability of the design ideas mentioned above to materials and devices is the extent to which the properties of an unsaturated motif can be predicted from those of the sp\(^2\) hydrocarbon with the same set of bare carbon centres. Does this model calculation suffice or must we use calculations that also include the (potentially

![Figure 1. Schematic of the graphane sheet. Shaded spheres correspond to hydrogen centres in axial CH bonds pointing out from the median plane towards the viewer, and white spheres to those in CH bonds that point away.](http://rspa.royalsocietypublishing.org/Downloaded from http://rspa.royalsocietypublishing.org/)
extensive) saturated environment? Here, we use comparative analysis of current-density maps for nanographanes and the corresponding sp² hydrocarbons to address this question. The maps will be computed by the ipso-centric method, which, as we explain below, is ideally suited for this analysis as it allows a breakdown of currents into well-defined molecular orbital contributions.

The structure of the paper is as follows. After a note on notation, a brief review is given of the ipso-centric method, its applications to aromatic systems, and its role in providing selection rules and orbital explanations for ring current that are robust to changes in level of theory. In the remainder of the paper, the ipso-centric method is applied to selected nanographanes and shown to give a general rationale for the similarity of the predicted ring currents to those in the corresponding sp² hydrocarbon. The printing/etching analogy is therefore useful, and can be used to design patterns of delocalization and current flow. Similar conclusions are shown to apply for an alternative functionalization where hydrogen is replaced by fluorine, and for an alternative architecture of the carbon sheet, where the requirement for all-chair rings and fully antiperiplanar hydrogenation is relaxed.

2. Notation

Some extra notation may be useful. The nanographene (benzenoid) and its hydrogenated derivative share a common molecular graph \( G \) representing the carbon framework: \( G \) has \( n \) vertices (carbon centres) and \( m \) edges (carbon–carbon \( \sigma \) bonds), with \( n = n_2 + n_3 \) and \( m = n_2 + 3/2n_3 \), where \( n_i \) is the number of carbon centres with exactly \( i \) carbon neighbours. The molecular formula of the nanographene is then

\[
C_nH_{n_2},
\]

and the formula of the fully saturated nanographane is

\[
C_nH_{2n_2+n_3}.
\]

A partially hydrogenated intermediate system can be seen as arising by formal deletion of one hydrogen from each of \( p \) carbon centres of the fully saturated system (2.2), or addition of one hydrogen to each of \( n - p \) carbon centres of the nanographene (2.1), to give formula

\[
C_nH_{2n_2+n_3-p}.
\]

Typically, the resulting set of \( p \) sp² carbon centres will itself correspond to the skeleton \( G' \) of a chemically interesting annulene, benzenoid or disjoint union of such molecules. Our comparison is then between the properties of the whole system (2.3) with sp³ carbons forming subgraph \( G - G' \), and sp² carbons forming subgraph \( G' \), and those of the isolated molecule(s) with sp²
graph $G'$. We can think of the intermediate system (2.3) as formally equivalent to the sp$^3$ nanographane (2.2) with the molecules some sp$^2$ system ‘carved out’, i.e.

$$C_nH_{2n_2+n_3} - p \equiv C_nH_{2n_2+n_3}/C_{p'}H_{q'}, C_{p''}H_{q''}, \ldots$$

(2.4)

with $p' + p'' + \cdots = p_2 + p_3 = p$ and $q' + q'' + \cdots = q + p_2$, where $q$ is the number of edges in $G$ between $G - G'$ and $G'$, i.e. the number of hydrogens needed to replace dangling $\sigma$ bonds in the molecules when they are cut out of the nanographane, and $p_i$ is the number of vertices in $G'$ that had degree $i$ in $G$. For example, coronene with hydrogenation of the central hexagonal ring would be

$$C_{24}H_{24} \equiv C_{24}H_{42}/C_{18}H_{18},$$

whereas coronene with hydrogenation of all except one hexagonal ring would be (one of two isomers of)

$$C_{24}H_{36} \equiv C_{24}H_{42}/C_{6}H_{6},$$

indicating that the appropriate comparisons of current patterns would be with [18] annulene and benzene, respectively.

3. Theoretical background

Aromaticity is a notoriously ill-defined but useful chemical concept [23]. One stream of thought [24,25] links aromaticity of benzene, and by extension other cyclic conjugated $\pi$ systems, to the ability of a system to support a ring current in the presence of an external magnetic field. On this definition, an aromatic system is one that supports a diatropic current, circulating in the same sense as in benzene, and an antiaromatic system is one that supports a current circulating in the opposite, paratropic sense. Experimentally, these currents are, in principle, detectable by their contribution to chemical shifts, albeit convoluted with numerous other effects. Theoretically, they can be calculated directly via perturbation theory. Assignment of aromaticity then reduces to visual inspection of a map of induced ($\pi$) current density. In principle, this is a straightforward problem as the perturbation equations are well known [26], but, in practice, the results for magnetic properties vary wildly with the choice of origin of vector potential. Much effort was devoted to avoiding or finessing this problem.

After the problem had vexed finite-basis computations of currents and derived quantities for many years, it was finally solved in an effective way by the distributed-origin Ansatz of Keith & Bader [27], one version of which [28] is the basis of our approach [29]. In the ipsocentric approach (also called CSGDT [27] and CTOCD-DZ [30]), calculation of total magnetic properties is reduced to the calculation of two first order perturbed wave functions, one with a linear momentum and one with an angular-momentum perturbation operator [29]. The current at a given point in molecular space is calculated with that point taken as the origin. As has been discussed in several places [31], this choice has computational advantages in that well converged results are obtained with modest basis sets [32], with unique and straightforward partition into non-redundant orbital contributions [29] that depend only on the (free) choice of MO basis for the zero-field calculation. This flexibility itself can be exploited to test for intrinsically delocalized magnetic response [33]. For a system such as benzene, the global $\pi$ ring current emerges as the contribution of just two canonical molecular orbitals (CMOs; the HOMO pair), whereas with a set of localized molecular orbitals (LMOs) all three are required to reproduce the current; by contrast, the localized $\pi$ currents of borazine each represent the contribution of a single LMO, whereas all three $\pi$ CMOs are needed to recover the full pattern in the canonical picture. In this work, we encounter current patterns of mixed character, where several spatially separated ring currents can coexist in a large molecule. In such cases, LMO contributions give the most economical account of this ‘local delocalization’.
For the purposes of interpretation, the orbital contributions associated with the ipsocentric method have a major conceptual advantage. As proved in [29], this particular choice of origin implies that the perturbed molecular orbitals can be expanded as double sums over states in which the electronic perturbation operators are respectively the linear momentum (replacing the diamagnetic term) and the angular momentum (replacing the paramagnetic term). This leads immediately to a frontier-orbital selection-rule picture of the connection between current and electronic structure in which the induced current is a result of virtual excitations between occupied and unoccupied orbitals. Global symmetry rules then apply: the perturbation operators for a planar system have the symmetries of in-plane translations \((T_x, T_y)\) for the case of linear momentum, and of the in-plane rotation \((R_z)\) in the case of angular momentum. When CMOs are used, the non-zero contributions to diatropic current arise from virtual excitations for which the product of representations of initial orbital, final orbital and perturbation operator contains a totally symmetric component, i.e.

\[
\Gamma(\psi_{\text{occ}}) \times \Gamma(\psi_{\text{unocc}}) \times \Gamma(T_x, T_y) \supset \Gamma_0.
\] (3.1)

Likewise, non-zero contributions to paratropic current arise when the product of representations contains a totally symmetric component, i.e.

\[
\Gamma(\psi_{\text{occ}}) \times \Gamma(\psi_{\text{unocc}}) \times \Gamma(R_z) \supset \Gamma_0.
\] (3.2)

In the sum-over-states formulation, the contribution of any symmetry-allowed excitation is further modulated by an energy denominator that depends on the separation in energy of the corresponding occupied and virtual orbitals. This has the effect of reinforcing dominance of frontier-orbital contributions. In the simplest cases, essentially the whole of the induced \((\pi)\) current is accounted for by HOMO–LUMO excitations. The clearest instance of HOMO–LUMO dominance occurs for planar annulenes, where the symmetry selection rules reduce to node counting [34]. From the association between \(\pi\) molecular orbitals, axial quantization of angular momentum and patterns of angular nodes, it is easy to see that \(\pi–\pi^*\) virtual excitations contribute diatropic current when the occupied \(\pi\) and empty \(\pi^*\) orbitals differ by 1 in angular node count, and paratropic current when the occupied \(\pi\) and empty \(\pi^*\) have the same angular node count.

The consequence is that planar and planar-constrained [\(n\)]annulenes with \((4N + 2)\) \(\pi\) electrons have a diatropic \(\pi\) ring current arising essentially entirely from the HOMO–LUMO excitation, and [\(n\)]annulenes with \(4N\pi\) electrons have a paratropic \(\pi\) ring current dominated by the HOMO–LUMO excitation across the gap opened up by Jahn–Teller distortion, with partial cancellation by the weaker diatropic (HOMO – 1)–LUMO and HOMO–(LUMO + 1) excitations [34].

Extended versions of these symmetry and orbital-topology-based arguments have been used in the interpretation of current-density maps for systems exhibiting conventional, multiple, hetero, all-metal, transition-state and other types of aromaticity [35–39]. Considerations of this type have helped to explicate the complex patterns of current in nanographenes, where currents arising from Clar sextet contributions to electronic structure coexist with global perimeter ring currents [40].

The node-counting approach remains useful even in low-symmetry situations if the local topology of the frontier orbitals is retained, and so will be a valuable tool for analysis of currents in the nanographanes to be discussed later in this paper.

### 4. Calculations

To investigate this printing/etching analogy, geometries for a selection of graphene/graphane hybrids (excluding the model systems of [18] and [22] annulene and [6] radialene, which were treated separately in a manner explained below) were optimized at the B3LYP/6-31G** level using the Gaussian09 package [41]. These structures were confirmed as local minima on the potential energy surface by calculation of vibrational frequencies. For cartesian coordinates, see electronic supplementary material.
Annulene and radialene models were constructed as follows. To construct the model $D_{6h}$ \[18\] annulene and $D_{2h}$ \[22\] annulene, we take $D_{6h}$-optimized coronene and $D_{2h}$-optimized ovalene and delete the interior sp$^2$ cycles and replace them with hydrogens positioned at 1.08 Å along the carbon–carbon bond vectors formerly connecting them to the perimeter. The model \[6\] radialene in its energetic minimum possesses a heavily distorted tub-shaped structure. To give a useful comparison with the related nanographane, in which the etched sp$^2$ region is restricted to a relatively planar geometry by its sp$^3$ framework, the free radialene model was optimized with fixed $D_{6h}$ symmetry, which resulted in a planar structure with three imaginary vibrational modes (a single mode at $152i\,\text{cm}^{-1}$ and a pair at $123i\,\text{cm}^{-1}$).

Current-density maps were calculated for nanographane systems and models using the ipsocentric method at the CHF/6-31G** level using the SYSMO package \[42\]. This basis, though relatively modest, is sufficient for the calculation of current-density maps, as the efficient ipsocentric approach gives rapid convergence with basis set \[32\], having effectively reached the basis limit for carbon networks at this level. All current maps are plotted in a plane 1 $a_0$ above the median plane of the sp$^2$ carbon centres and aromaticity/antiaromaticity is diagnosed by observation of anticlockwise/clockwise circulations of induced ring current, corresponding to diatropic and paratropic ring currents, respectively. To enable quantitative discussion of the intensities of the induced currents, the maximum modulus of current density in the plotting plane, $j_{\text{max}}$, is compared with the values of related molecules or reference systems such as benzene ($j_{\text{max}} = 0.079$ atomic units (a.u.)) calculated at the same level.

The standard methodology that we employ uses DFT to find optimum molecular geometries but coupled Hartree–Fock theory to calculate magnetic response. This combination has been shown \[43\] to produce consistent results, avoiding the broken-symmetry geometrical structures that can sometimes occur in Hartree–Fock optimizations, and the exaggeration of magnetic response that can arise from underestimation of HOMO–LUMO gaps in DFT approaches to the calculation of response properties \[44\]. In practice, the replacement of HF- by DFT-perturbed densities has little effect \textit{per se} on current-density maps at the qualitative level. When there is an effect, it is typically a consequence of the change in underlying geometry. In this paper, we tested the robustness of our calculations by producing current maps for several coronene-based nanographenes consistently at the DFT level, i.e. using B3LYP/6-31G** perturbed densities for the ipsocentric calculations \[45\] at the B3LYP/6-31G** optimum geometries, using the GAMESS-UK package \[46\] linked to SYSMO \[42\]. As the maps in figure 3 show, there is no qualitative effect on current patterns, which leaves the printing/etching analogy with annulenes fully intact.

In rigorously planar systems, contributions to $\pi$ current can be easily identified using symmetry. The nanographanes of interest in this work, however, are non-planar, and therefore $\pi$ symmetry is not strictly maintained. Localization of molecular orbitals using the Pipek–Mezey \[47\] localization procedure enables the identification of occupied ‘$\pi$’ orbitals from the inspection of orbital and current plots. These contributions are then summed to produce a map of ‘total $\pi$’ current, which can also be obtained by similar analysis of CMOs. In more complex systems, local sums of LMOs can be used to recover individual physically separated delocalized regions, e.g. 12–14, to be discussed below.

5. Nanographanes based on coronene

(a) Current-density maps

As a first example, we consider the nanographane modification of a small and highly symmetrical benzenoid, coronene. There are three symmetrical possibilities (figure 3): we can hydrogenate the central benzene ring or fully or partially hydrogenate the perimeter to give $D_{3d}$ species 1 ($C_{24}H_{42}/C_{18}H_{18}$), 2 ($C_{24}H_{42}/C_{6}H_{6}$) and 3 ($C_{24}H_{42}/C_{12}H_{12}$), mimicking \[18\] annulene, benzene and \[6\] radialene patches carved into the graphene environment.

The lowering of symmetry from $D_{6h}$ to $D_{3d}$ leaves sp$^2$ frameworks that are effectively planar in the cases of 1 and 2. At the B3LYP/6-31G** level used here, the maximum vertical deviation
Figure 3. Three nanographanes formally derived from coronene by hydrogenation of the central ring, full or partial hydrogenation of the perimeter: (a) \(1 (C_{24}H_{42}/C_{18}H_{18})\); (b) \(2 (C_{24}H_{42}C_6H_6)\) and (c) \(3 (C_{24}H_{42}C_{12}H_{12})\). The first column shows the schematic molecular structures. The second column shows the \(\pi\) ring current maps calculated at the ipso-centric CHF/6-31G** level for structures optimized at the B3LYP/6-31G** level. The total \(\pi\) currents in these maps are defined by superposition of localized molecular orbital (LMO) contributions, chosen as described in the text. The third column shows the corresponding total \(\pi\) currents in annulene (or, in (c), radialene) model systems. The final column shows total \(\pi\) currents calculated as for column 2 but replacing CHF perturbed densities by B3LYP. Standard plotting conventions are used (see text).

from the mean plane of the sp\(^2\) region of the molecule is \(\pm 0.06 \text{ Å}\) for the annulene of \(1\), and \(\pm 0.01 \text{ Å}\) for the benzene ring of \(2\). Retention of delocalization is also indicated by the uniform sp\(^2\)–sp\(^2\) bond lengths (12 \(\times\) 1.401 Å and 6 \(\times\) 1.406 Å in \(1\); 6 \(\times\) 1.411 Å in \(2\)). The radialene patch of \(3\) has a near-planar C\(_6\) ring (vertical deviation \(\pm 0.03 \text{ Å}\), bond lengths 1.480 Å) with exo CC bonds (1.358 Å) bent out of plane (deviation \(\pm 0.21 \text{ Å}\)). The geometries already indicate retention of delocalization in the sp\(^2\) frameworks of \(1\) and \(2\) but localization towards exo double bonds in \(3\). The \(\pi\) current-density maps constructed using LMOs as described above are shown in figure 3, where they are compared with free-molecule models.

As is clear from the maps, \(1\) and \(2\) support delocalized (diatropic) currents flowing around the circuits of sp\(^2\) centres, comparable in strength with the ring currents in the free-molecule model systems, which are themselves similar to the currents in the fully relaxed systems (values of \(j_{\text{max}}\) calculated at 1 \(a_0\) above the median plane of the sp\(^2\) centres are 0.187 a.u. for \(1\) and 0.078 a.u. for \(2\) cf. 0.178 a.u. and 0.078 a.u. for the annulene model and for benzene, respectively). Nanographane \(2\) therefore supports a full benzene ring current, and the larger circuit of nanographane \(1\) has a current that is more than twice as strong. The radialene-like system, \(3\), however shows only weak, localized currents in the bonds exo to the central ring. Three of the bonds point away from the median plane and hence the plotting plane above it, and so only the three upper bond circulations are visible in figure 3 but three exactly identical features are of course found in a plotting plane of \(-1 \, a_0\), and all six features are visible in a single plotting plane for the D\(_{6h}\)-constrained [6] radialene, which is known to have localized magnetic response rather than to have a ring current [48].
Figure 4. Orbital energy-level diagram showing the first three $\pi - \pi^*$ excitations from the degenerate HOMO pairs of 1 (a) and an [18] annulene model, 4 (b). Canonical molecular orbitals are shown, with orbital energies in $E_h$; general conventions for excitations are dominant excitations shown in bold, translationally allowed excitations shown as narrow, solid arrows, and rotationally allowed excitations (not seen in this figure) as wide, hollow arrows.

The final column of figure 3 shows the effect of replacing the CHF ipsocentric calculation by a fully consistent B3LYP DFT calculation of current density [45]. As a comparison of columns 2 and 4 of the figure will confirm, the maps are hardly affected by this change in the level of theory. This is to be expected, because, as discussed below, the qualitative pattern of current and its similarity to the currents in the annulene and radialene models are essentially determined by orbital nodal topologies. Nodal character of the frontier orbitals does not change at the DFT level.

(b) Orbital interpretation of currents

The similarity in overall patterns of current between nanographanes and models of free molecules is striking, and perhaps expected on structural grounds, but it can be given a deeper explanation. It can be traced to the retention in the nanographane of nodal patterns and approximate symmetries of the orbitals of the $\pi$ system of the isolated molecule. When a $\pi$ system is delocalized, as it is here, an analysis in terms of CMOs is revealing [33]. Figure 4 compares the CMOs and their contributions with current for [18] annulene in a model geometry derived from coronene, 4, with those for the nanographane 1.

As figure 4 shows, there is a one-to-one correspondence between the CMOs of 1 and those of the [18] annulene. Although the frontier orbitals of 1 show some small central features associated with symmetry-allowed admixture of local CH bonds, they retain a clear angular-momentum assignment: a HOMO pair with an effective angular-momentum quantum number $\Lambda = 4$ (eight sign changes in the perimeter), lies below a LUMO pair with $\Lambda = 5$ and a split pair of higher $\pi^*$ orbitals with $\Lambda = 6$, as in the annulene. In full cylindrical symmetry, the only allowed orbital contribution to $\pi$ ring current would arise from the HOMO–LUMO virtual excitation, and would be diatropic. In the finite point groups of 1 and its annulene model, further (weaker) excitations become allowed, again contributing diatropic current as they are translational in nature. The HOMO orbital contributions in 1 and in the annulene dominate the total $\pi$ current and arise from essentially pure HOMO–LUMO excitations. The retention of a few-electron, annulene-like current in 1 is therefore fully compatible with the deduction from the ipsocentric
Figure 5. The smallest loops of diatropic and paratropic current enclosing graphene islands: the $(4N + 2)$ pyrene-like 5 \((a)\), and $(4N)$ phenalene-like 6 \((b)\), perimeters. The right-hand side of each panel shows a map of total $\pi$ current obtained by the LMO superposition procedure and drawn using the standard plotting conventions, as described in the text. Bond lengths (in Å) calculated at the B3LYP/6-31G** level are reported on the schematic on the left and a side on view of the structure is shown at the bottom of the panel.

approach, given the preservation of the nodal structure of the frontier $\pi$ orbitals. This qualitative interpretation is confirmed by the near quantitative match in $j_{\text{max}}$ values between the maps of total $\pi$ current (0.187 a.u.) and of the HOMO pair contribution (0.178 a.u.), in spite of the fact that the first is calculated with localized, and the second with canonical, orbitals.

A similar analysis can be applied to 2, where the central ring current arises predominantly from the HOMO–LUMO $\Lambda = 1–2$ virtual excitation responsible for the current in benzene [29,34]. By contrast, the six localized $\pi$ current loops of 3 are individually ascribable to local $\pi$ to $\pi^*$ excitations and can only be recovered in the CMO picture by superposition of the full set of occupied orbitals. This is as expected from the magnetically localized nature of 3 and is again compatible with the published analysis of the model [6] radialene [48].

6. Diatropic and paratropic currents in nanographanes

This discussion of nanographanes based on coronene has revealed some design principles which can be applied to construct current patterns of arbitrary complexity. The smallest building blocks of diatropic and paratropic currents enclosing graphene islands are evidently those derived from pyrene and phenalene perimeters, respectively, as these are the smallest non-trivial $(4N + 2)$ and $(4N)$ circuits in graphene. Figure 5 shows schematic structures and patterns of $\pi$ current for the two nanographanes 5 (C$_{16}$H$_{26}$/C$_{14}$H$_{14}$), and 6 (C$_{13}$H$_{22}$/C$_{12}$H$_{12}$), which as noted above are not necessarily the global optima for C$_{16}$H$_{12}$ and C$_{13}$H$_{10}$, respectively. (In the experimental isomer of phenalene, C$_{13}$H$_{10}$, one of the perimeter carbons carries two hydrogen atoms and the central carbon none, for example).

Central hydrogenation of pyrene to give 5 leads to a structure of C$_{2h}$ symmetry with near-uniform perimeter bond lengths (maximum deviation 0.01 Å) and a near-planar geometry of the sp$^2$ carbon framework (deviation ± 0.06 Å). The diatropic current of the dihydropyrene (5) is readily rationalized in terms of the analogy with a delocalized C$_{2h}$-constrained [14] annulene, and again arises essentially from node-increasing excitations between $\Lambda = 3$ HOMO and $\Lambda = 4$ LUMO pairs, each of which is split into two components under C$_{2h}$ symmetry.

Construction of a closed-shell C$_{13}$H$_{10}$ nanographane system by formal hydrogenation at the central atom of the phenalenyl radical leads to a structure with reduced C$_3$ point-group symmetry. The perimeter bonds show pronounced single/double alteration (±0.10 Å) as expected for an antiaromatic 12 $\pi$ system undergoing Jahn–Teller distortion from ideal C$_{3v}$ symmetry, but the unsaturated carbon framework remains essentially planar (heights within an interval of 0.14 Å).
Figure 6. Energy-level diagram and contributions of canonical molecular orbitals (CMOs) to \( \pi \) current in 6: (a) frontier CMOs and the associated \( \pi - \pi^* \) excitations, showing the dominance of the rotationally allowed HOMO–LUMO transition and (b) paratropic \( \pi \) current contribution of the HOMO; (c) diatropic \( \pi \) current contribution of the degenerate HOMO-1 pair. Orbital energies are given in \( E_h \) and standard plotting conventions (see text) are used for the maps.

Paratropic currents have a more subtle explanation than diatropic currents in the ipso-centric approach. The dominant contribution is paratropic in character and arises from the rotational HOMO–LUMO excitation across a split angular-momentum pair (\( \Delta \Lambda = 0 \)); this is inevitably accompanied by a translational diatropic contribution from HOMO-1 to LUMO (\( \Delta \Lambda = +1 \)). In the present case, figure 6 shows the frontier orbital energy-level diagram for 6 in which we see the non-degenerate HOMO and LUMO, both corresponding to \( \Lambda = 3 \) in idealized full cylindrical symmetry, where they would be interconverted by a rotation of \( \pi / 6 \) about the principal axis. In the \( C_3 \) group, they are each of \( A \) symmetry and remain approximately rotationally equivalent, although split in energy. The HOMO-1 pair corresponds to \( \Lambda = 2 \) and is of \( E \) symmetry in the \( C_3 \) group. Therefore, in 6, the dominant rotationally allowed \( \Delta \Lambda = 0 \) HOMO–LUMO transition (\( A-A \)) gives the paratropic contribution and the translationally allowed (HOMO-1)–LUMO \( \Delta \Lambda = +1 \) transition (\( E-A \)) across a larger energy gap gives a much weaker diatropic perimeter current (figure 6). This pattern of strong paratropic current with partial cancellation from a weak diatropic contribution is characteristic of planar geometries of antiaromatic \([4N]\) annulenes, where the separation of HOMO and LUMO arises from a Jahn–Teller splitting \([34]\). The total \( \pi \) current in 6 (figure 5), is therefore most simply interpreted as a strong paratropic \( \pi \) HOMO contribution (figure 6b) partly damped by weaker diatropic contributions (figure 6c). This interpretation is supported by the \( j_{\text{max}} \) values of 0.110, 0.145 and 0.042 a.u. obtained from the total \( \pi \), HOMO and HOMO-1 maps, respectively.

7. Ring current patterns by design

Given the success of the analogy between cycles of sp\(^2\)-hybridized carbon in ‘etched’ graphanes and free annulenes, we can hope to apply the same design principles more widely to additional conjugated patches and model systems, and to more complex patterns of conjugation. Figure 7 shows further examples illustrating the etching of an annulene-like current pattern in a nanographane. The examples illustrate benzene-like (7) and naphthalene-like (8) circuits in unsymmetrical positions, and a centrally positioned anthracene circuit (9), all derived formally from coronene, and symmetrical naphthalene (10) and [22] annulene (11) circuits derived from ovalene. Each of these nanographane systems shows near planarity of the sp\(^3\) region and a narrow distribution of bondlengths consistent with substantial electron delocalization.

Total \( \pi \) currents calculated by the procedure of identifying suitable LMOs are shown for all cases, and in every case display the hoped-for similarity to the related annulenes and polyacenes (figure 8). The analogy extends to the analysis of orbital contributions and need not be given in detail here. For anthracene, the map shares the same feature of larger current in the central part of the perimeter found for the free molecule, which has been called the ‘anthracene problem’, and has been shown to be a feature of molecular orbital and conjugated circuit treatments alike \([49]\).
Figure 7. A further three nanographanes formally derived from coronene by partial hydrogenation of the perimeter: C\textsubscript{2} symmetric 7 (C\textsubscript{24}H\textsubscript{42}/C\textsubscript{6}H\textsubscript{6}); C\textsubscript{2h} symmetric 8 (C\textsubscript{24}H\textsubscript{42}/C\textsubscript{10}H\textsubscript{8}); C\textsubscript{2h} symmetric 9 (C\textsubscript{24}H\textsubscript{42}/C\textsubscript{14}H\textsubscript{10}); C\textsubscript{2h} symmetric 10 (C\textsubscript{32}H\textsubscript{56}/C\textsubscript{10}H\textsubscript{8}); C\textsubscript{2h} symmetric 11 (C\textsubscript{32}H\textsubscript{56}/C\textsubscript{22}H\textsubscript{22}). Rows (a,c) show the schematic structures of the five systems, rows (b,d) their \pi ring currents obtained by the LMO superposition procedure. Standard plotting conventions (see text) are used for the maps. Unique bondlengths (in Å) of interest are: a, 1.415; b, 1.407; c, 1.399; d, 1.387; e, 1.437; f, 1.389; g, 1.434; h, 1.435; i, 1.432; j, 1.379; k, 1.406; l, 1.416; m, 1.372; n, 1.442; o, 1.448; p, 1.412; q, 1.434; r, 1.369; s, 1.439; t, 1.408; u, 1.407; v, 1.401; w, 1.402; x, 1.406; y, 1.404; z, 1.406.

The same design principles can be applied to produce patterns with multiple closed circulations. Three examples are shown in figure 9, two showing paired diatropic circulations and one a pair of paratropic currents.

In 12, two phenanthrene-like regions are constructed by partitioning ovalene with a central strip of sp\textsuperscript{3} carbon centres. Each of the two independent currents follows a phenanthrene pathway and is of similar strength to that of the isolated molecule (j\textsubscript{max} = 0.101 a.u. for 12 and 0.092 a.u. for phenanthrene itself).

In 13, the isolation of a perylene-like sp\textsuperscript{2} region produces a pair of diatropic circulations. Here, the separation of the two currents is a consequence of the internal electronic structure of the sp\textsuperscript{2} region: perylene itself shows two almost independent naphthalene-like currents, a
Figure 8. Map of $\pi$ current density for the [22] annulen model of 11. As the molecule is rigorously planar, CMOs and LMOs give identical maps. Standard plotting conventions are used (see text).

Figure 9. Examples of nanographanes that exhibit multiple closed circulations: (a) $C_{2h}$ symmetric 12 ($C_{32}H_{56}/C_{14}H_{10}$, $C_{14}H_{10}$); (b) $C_2$ symmetric 13 ($C_{32}H_{56}/C_{10}H_8$, $C_{10}H_8$); (c) $C_i$ symmetric 14 ($C_{34}H_{50}/C_{12}H_{22}$, $C_{12}H_{22}$). Schematic structures are shown in the left-hand column, $\pi$ ring current maps produced by the localization procedure in the right-hand column. The standard plotting convention used is detailed in the text. Unique bond lengths (in Å) of interest are: aa, 1.343; ab, 1.348; ac, 1.410; ad, 1.361; ae, 1.411; af, 1.368; ag, 1.417; a, 1.448; b, 1.398; c, 1.382; d, 1.415; e, 1.419; f, 1.377; g, 1.412; h, 1.396; i, 1.427; j, 1.428; k, 1.428; l, 1.398; m, 1.422; n, 1.470; o, 1.455; p, 1.354; q, 1.455; r, 1.353; s, 1.462; t, 1.363; u, 1.460; v, 1.362; w, 1.461; x, 1.354; y, 1.453; z, 1.356.

The fact that is easy to understand on a conjugated-circuit model, as all nine Kekulé structures of perylene have formal single bonds on the two perimeter edges of the central ring [21,29,50]. The separation into two circulations is advanced in 13 by geometrical factors: the two naphthalene
Figure 10. Energy-level diagram and contributions to π current in 14: (a) frontier canonical molecular orbital and the associated π − π * excitations, showing the dominance of rotationally allowed HOMO–LUMO and (HOMO − 1)−(LUMO + 1) transitions; (b) paratropic π current contribution of the six localized molecular orbitals that correspond to the left-hand phenalene fragment. Orbital energies are given in E_h and standard plotting conventions (see text) are used for the maps.

fragments are twisted by approximately 10° (local median plane to local median plane), which again indicates reduced double bond character in the linking edges, and accounts for the apparent left–right asymmetry in the map shown in figure 8, where the plotting plane is parallel to the sp²-median plane.

Finally, the map for nanographane 14 shows that disjoint paratropic circulations can exist in closed-shell systems. Two phenalene subunits are produced using a separating strip of hydrogen atoms in conjunction with internal hydrogenation. They each support a ring current mimicking the free system 6. The full nanographane system 14 as a whole has C_i point-group symmetry, but the map appears less symmetric owing to the twisting of the two 12 π circuits with respect to each other and to the plotting plane (1 a₀ from the median plane of the sp² centres).

The map in figure 9c shows the total π current. This can be partitioned in different ways. For a delocalized π system, we can expect that the total current can be accounted for with a small number of contributions from CMOs. As figure 10a shows, the occupied and unoccupied frontier orbitals of 14 derive from in- and out-of-plane combinations of the respective frontier orbitals of the two phenalenyl fragments. Four HOMO–LUMO virtual excitations are allowed in C_i symmetry: the ‘diagonal’ A_g–A_g and A_u–A_u excitations have rotational character and the ‘off-diagonal’ A_g–A_u and A_u–A_g excitations have translational character. The diagonal contributions involve simultaneous rotational excitation on each fragment, and hence dominate the contribution from the HOMO pair leading to the observed strongly paratropic overall current. The net contributions from the HOMO-2 to HOMO-5 CMOs are a pair of weak diatropic currents on the fragments consistent with local translational excitations. The current therefore is economically represented by six CMOs spread over the whole molecule. An alternative representation can be formed from the six LMOs associated with one phenalene fragment (figure 10b). The map separates neatly into two circulations, supporting our claim that 14 is an example of a locally delocalized π system: two delocalized sp² circuits separated by an insulating sp³ region, as envisaged in the printing/etching analogy.

8. Other modification of nanographanes

All examples shown so far have been constructed by hydrogenation of the graphene sheet in a manner that is consistent with the all-chair form of graphane. Both fluorinated analogues of graphane, and configurational isomers of graphene, have featured in literature reports, and it is of interest to check whether the printing/etching analogy survives chemical and structural variations of this kind.
Figure 11. Two perfluoro nanographanes formally derived from coronene: (a) 1a (C_{24}F_{42}/C_{18}F_{18}) and (b) 2a (C_{24}F_{42}/C_{6}F_{6}). The first column shows the schematic molecular structures. The second column shows the \( \pi \) ring current maps calculated at the ipsocentric CHF/6-31G** level for structures optimized at the B3LYP/6-31G** level, defined by superposition of LMO contributions. Plotting conventions as described in the text.

(a) Perfluoro nanographanes

To test sensitivity to chemical substitution, calculations in which all hydrogen atoms of the nanographane were replaced by fluorine atoms were carried out for 1 and 2, the two symmetrical ‘aromatic’ nanographane derivatives of coronene, to produce 1a and 2a, respectively.

Replacement of hydrogen with fluorine leads to small changes in geometry of the sp\(^2\) regions in 1. Vertical deviation of the 18 carbon perimeter increases from ±0.06 Å (1) to ±0.10 Å (1a), and dispersion in perimeter bond lengths increases slightly, with the long bonds extending from 1.406 Å (1) to 1.408 Å (1a), and the short bonds shortening from 1.401 Å (1) to 1.393 Å (1a). D\(_{3d}\) symmetry is retained. Changes in the ring-current are also small: the currents for 1 and 1a in figure 3 and figure 11 are essentially visually indistinguishable.

A similar picture is found on comparison of 2 and 2a, where the perfluoro analogue has a reduced symmetry (S\(_6\)) corresponding to distortion along a low-energy A\(_{2g}\) mode of an idealized D\(_{3d}\) structure. The C\(_6\) ring has negligible vertical deviation in 2a (approx. 0.001 Å) and a uniform bond length of 1.408 Å (cf. 1.401 Å in 2). Again, the ring current in 2a, like that in 2, is satisfyingly similar to that of benzene itself.

(b) Alternative configurational isomers

As an initial exploration of sensitivity to the conformation of the underlying carbon framework, two forms of the nanographane produced by full hydrogenation of coronene were constructed (figure 12). Consistent antiperiplanar hydrogenation leads to the all-chair form; hydrogenation where each CH bond is involved in one eclipsing interaction leads to the all-boat form. Removal of one hydrogen atom at each peripheral site leads either to D\(_{3d}\) 1 or to C\(_{2v}\) 1b, where the central hexagonal ring has a boat conformation. The 18 carbon sp\(^2\) cycle in 1b has uniform bond lengths (all 1.400 ± 0.001 Å) and a larger vertical range of 0.26 Å (cf. 0.01 Å in 1), but still supports annulene-like ring current (figure 13).
Figure 12. Alternative all-chair (a) and all-boat (b) conformations of the carbon framework in a nanographene as imposed by suitable choices of hydrogenation pattern.

Figure 13. (a,b) Two nanographanes formally derived by selective dehydrogenation of a coronane fragment of the all-boat graphene sheet (figure 12). The first column shows the schematic molecular structures. 1b and 2b share formulae C_{24}H_{42}/C_{18}H_{18} and C_{24}H_{42}/C_{6}H_{6} with 1 and 2, respectively. The π ring current maps are calculated at the ipso-centric CHF/6-31G** level for structures optimized at the B3LYP/6-31G** level, defined by superposition of LMO contributions. Plotting conventions as described in the text.

Likewise, dehydrogenation of the central ring leads either to D_{3d} 2 or C_{2v} 2b. The central sp² region has near-uniform bond lengths (1 × 1.405 and 2 × 1.407 Å). In spite of the rumpling produced by unfavourable CH bond interactions around the perimeter, 2b still has an essentially planar central ring (height range 0.03 Å), with a typical benzenoid ring current (figure 13).

These preliminary calculations reinforce our expectation that the printing/etching analogy hitherto survives chemical and conformational changes as a useful design principle for π electron delocalization pathways in graphene/graphane hybrids.
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