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ARTICLE

Modelling Aromatisation of $(BN)_nH_{2n}$ Azabora-annulenes

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Despite a long tradition of descriptions of borazine as an 'inorganic benzene', this molecule is a non-aromatic species according to the magnetic (ring-current) criterion. Borazine, borazocine, and the larger neutral $(BN)_nH_{2n}$ azabora-annulene heterocycles in planar conformations, although π-isoelectronic with [2n]annulenes, support only localized induced currents in perpendicular magnetic fields. The π-current maps of these systems comprise superpositions of separate 'lone-pair' circulations on all nitrogen centres. For the systems with n>4, planarity must be enforced by a constraint. Qualitative orbital analysis based on the ipsocentric approach to calculation of induced current density suggests that global induced currents could be produced through strategic changes to the π electron count. In *ab initio* calculations, azabora-annulenes with rings of size [8]- and larger were indeed found to support global diatropic ring currents in both anionic and cationic forms with (4*N*+2) π electron counts. The planar conformation of the charged ring typically occupies a stationary point of higher order on the potential energy surface, rather than a minimum.. However, the borazocine dianion, $[B_4N_4H_8]^{2-}$, occupies a planar minimum, supports a diatropic ring current of strength comparable to that in benzene, and is predicted to participate in sandwich compounds; it is therefore a good candidate for an aromatised azabora-annulene.

Introduction

Borazine has, increasingly controversially, been considered an 'inorganic benzene', as have a number of similar systems with six-membered aromatic scaffolds.[1–15] Although borazine itself has the 'aromatic' (4*N*+2) π electron count, the magnetic properties of this molecule are consistent with non-aromaticity on the ring-current criterion. The ipsocentric approach for calculation of magnetic response gives a powerful scheme for partition of induced current density into non-redundant orbital contributions, governed by symmetry- and node-counting selection rules.[16,17] The ipsocentric approach also accounts for the qualitative difference between maps of π current for benzene and borazine.[4,7,18] This striking difference is a function of the reduced molecular symmetry and the greater localisation of π electrons in borazine. In the ipsocentric model, the *diatropic* currents in simple monocycles arise from occupied-unoccupied virtual transitions that have a product symmetry including the representation of an in-plane translation, which therefore corresponds to an increase of one in the count of nodal lines intersecting the π system, or equivalently in the quantum number for the axial component of angular momentum. For *paratropic* currents, the relevant symmetry is that of an in-plane rotation, which preserves node count. In D_{6h} benzene, π LOMO, HOMO, LUMO and HUMO (symmetries a_{2u}, e_{1g}, e_{2u} and b_{2g}, respectively) have clear even/odd angular-momentum parentage, and all π current arises from the purely diatropic π-HOMO to π-LUMO virtual transition induced by the external perpendicular magnetic field. In D_{3h} borazine, the π MO symmetries reduce to a_2'', e'',

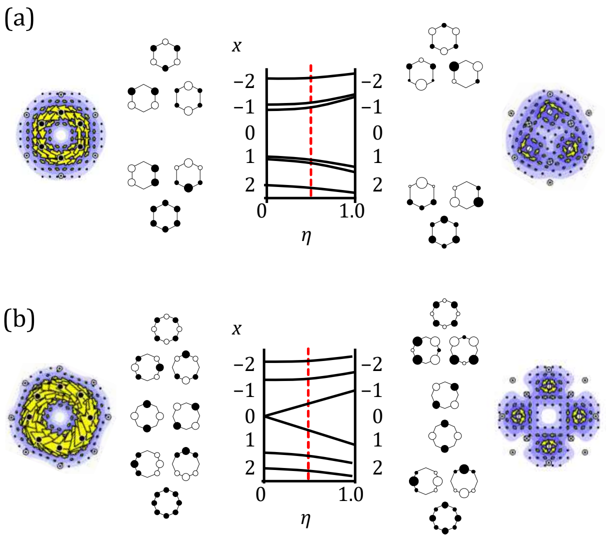

Figure 1: Schematic energy, orbital and current-density correlation diagrams for annulenes and azabora-annulenes. Working inwards, the figure shows current-density maps, Hückel molecular orbital composition and the orbital energy correlation diagram for formal conversion of an annulene to an azabora-annulene in the cases of (a) $B_3N_3H_6$ and (b) $B_4N_4H_8$. The Hückel calculations use a single electronegativity parameter, η, for the Coulomb parameters $\alpha_B = \alpha - \eta\beta$ and $\alpha_N = \alpha + \eta\beta$. The graphs (adapted from Ref. 4) show the variation of orbital energy, $x = (\varepsilon - \alpha)/\beta$. Maps of total π current density are shown in (a) benzene (left), and isoelectronic borazine (right), and (b) planar-constrained cyclooctatetraene (COT, left), C_8H_8, and isoelectronic planar borazocine, $B_4N_4H_8$, (right). The maps are calculated at the B3LYP/6-31G**//CHF/6-31G** level of theory, and plotted at a height of $1a_0$ above the plane of the molecule.

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e'' and a_2'', respectively and both π-LOMO and HOMO are sources of diatropic current. Crucially, however, the π-HOMO to π-LUMO virtual transition now has mixed translational and rotational character, allowing the possibility of a current flow that has mixed diatropic and paratropic character, which in borazine manifests as localised circulations on the electronegative N atoms.[4] These currents are diatropic with respect to the local atomic centre, but their outer parts are diatropic and their inner parts are paratropic with respect to the ring centre. Thus, the π current-density maps for borazine, calculated with the *ab initio* ipsocentric method, show localised circulations, rather than the global diatropic current that is diagnostic of aromaticity in benzene.[19] Similar conclusions about the pattern of ring current in borazine have been reached on the basis of molecular orbital contributions to the induced local magnetic field, itself a convolution of the induced current density.[20]

Localisation of magnetic response persists in the general case of planar $(BN)_nH_{2n}$ rings and in various related polycycles that are formally derived from benzenoids by partial or wholesale replacement of C_2 pairs with BN units.[21] Recently, this protocol of molecular design by successive substitution has been implemented on an impressive scale; substitution of C_2 pairs with BN in all possible ways in 77 Kekulean benzenoids generated >7 x 10^{12} distinct distinct hypothetical azabora-benzenoid hybrids, of which many were suggested as possible leads for application in light harvesting.[22]

A natural question arises. If borazine and its neutral congeners are non-aromatic, is there a systematic way to convert them into aromatics? In this paper we present a strategy for achieving this target.

Differences in ring-current response between isoelectronic CC and BN analogues can be rationalised using a very simple modified Hückel treatment that accounts for differences in electronegativity between neighbouring B and N atoms with a single adjustable parameter (η).[18] The frontier-orbital model of induced currents then explains the transition from delocalised to localised magnetic response for heterocycles. Bonding orbitals tend to concentrate on the electronegative centres, and anti-bonding on electropositive. In consequence, the field-perturbed orbitals, and hence the currents, become more localised, rendering the all-BN heterocycles non-aromatic on the magnetic criterion. In the ipsocentric approach, this trend is explained in terms of changes in strength of virtual transitions between occupied and unoccupied π frontier orbitals. Electronegativity differences leads to a widening of the π HOMO-LUMO gap and spatial separation of these molecular orbitals. These trends have been quantified in a parameterised *ab initio* model with non-integer nuclear charges that enables benzene to 'transmute' smoothly into borazine.[23]

The example of borazine shows that the simple numerical fact of a $4N+2$ π electron count is not a guarantee of ring-current aromaticity. It was found in a study of planar equilateral X_nY_n heterocycles with D_{nh} symmetry, where X and Y represent atoms or groups isolobal with the CH unit, that the differential electronegativity parameter, η, plays a crucial role in the balance between delocalisation and localisation of current.[18,24] Until the threshold for a significant paratropic contribution represented by $|\eta| \geq 0.5$ (see Figure 1), is reached, global diatropic currents are retained in the neutral system. In contrast, charged systems with $\eta \neq 0$ are expected to behave differently: π-excessive and π-deficient heterocycles occupy regions of the energy-level diagram far from the frontier that applies to π-sufficient systems, and in these cases both transition symmetry products and relevant energy gaps differ from those in the neutrals.

The schematic energy-level diagrams shown in Figure 1 explain why aromaticity is not to be expected for π-systems with relatively high values of η, such as azabora-annulenes, and also suggest a way to make these systems aromatic in a ring-current sense. Adjustment of the π frontier-orbital populations by two or four electrons for $4N$ and $4N+2$ systems, respectively, would lead to narrowing of the HOMO-LUMO gap at fixed η, thereby increasing the strength of the virtual excitations associated with induced ring-current. These considerations are based on simple Hückel theory and therefore neglect possible changes in electronic structure with charge. Their predictions will be confronted with calculations performed at a higher theoretical level in the present work.

The outline of the rest of the paper is as follows. First, the π current responses of D_{nh} planar constrained $(\mathrm{BN})_\mathrm{n}\mathrm{H}_{2\mathrm{n}}^{\mathrm{q}}$ ring systems, with n = 2 to 7 and q = 0, ±2 (for even n), and ±4 (for odd n), are presented and analysed in terms of orbital contributions. Then we are able to identify planar $[B_4N_4H_8]^{2-}$ as a new aromatic species supporting a fully developed diatropic ring current.

Methodology

Structures of the bare azabora-annulenes were obtained by optimisation of geometry at the B3LYP/6-31G** level using the Gaussian09 software,[25] and current-density maps were computed at the CHF/6-31G** level using the ipsocentric approach,[16,17] as implemented in the SYSMO and GAMESS-UK packages.[26,27] This combination of levels of theory has been shown to produce well-converged, consistent results, avoiding the broken-symmetry geometries that sometimes occur in Hartree-Fock optimisations.[28] The 6-31G** basis set is not large, but it is a specific advantage of the distributed-origin ipsocentric approach that currents are typically well converged for systems with even this modest number of functions.[29,30] Additional *ab initio* exploration of a $(B_4N_4H_8)_2Ti$ metallocene sandwich complex was carried out by optimisation of the geometry at the MP2/6-31G** level using the QChem 5.2 computational package.[31] All azabora-annulene structures were initially constrained to maximum D_{nh} symmetry, and the status of each calimed stationary point was confirmed by diagonalisation of the Hessian. Further calibration checks were carried out with the wB97X-2 long-range corrected exchange-correlation functional[31] to allow for possible systematic deficiencies of MP2. but these did not produce significant changes to geometry or character of stationary points of the azabora systems (see ESI).

The ipsocentric method,[16,17,32,33] gives physically realistic, readily interpretable currents at modest computational cost, and (uniquely) it allows the calculated current density to be partitioned into non-redundant orbital contributions, in both canonical (CMO)[30] and localised[19] (LMO) frameworks. The maps given in this paper show first-order current density (the first derivative of induced current with respect to the external magnetic field) in the plotting plane 1 a_0 above the plane of the nuclei. Arrows and contours show the vector current density resolved onto the plotting plane and the modulus of the current density, respectively. Nuclei at positions projected into the plotting plane, are represented by symbols, where H is ⊙, C is ◉, N is ⦶ and B is ⊗. The maximum magnitude of π-current density in the plotting plane, j_{max}, is a quantitative measure of the strength of the current in a given system. This value is usually referred to the benzene standard for the same plotting plane (0.078 a.u. at the present level of theory).[34]

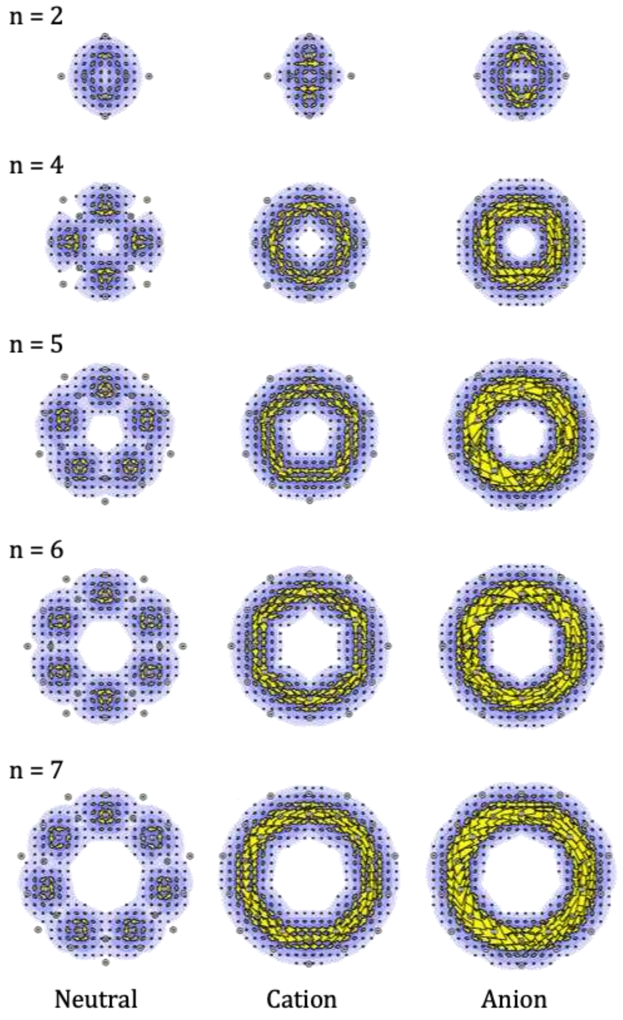

Figure 2: Total π current-density maps for D_{nh} planar constrained $(BN)_nH_{2n}{}^q$ ring systems, with n = 2 to 7 and q = 0, ±2 (for even n), or ±4 (for odd n). Species with n = 3 and $q \neq 0$ do not converge as (2n-q)π systems and are omitted. Plotting conventions are described in the text.

Results

Azabora-annulenes $(BN)_nH_{2n}{}^q$

The ring systems, $(BN)_nH_{2n}{}^q$, with n = 2 to 7 and q = 0, ±2 (for even n) and ±4 (for odd n), were optimised under the constraint of D_{nh} planar symmetry. Figure 2 shows the calculated total π-current density maps for all but the cases based on borazine itself (for reasons explained below). The symmetry-constrained neutral heterocycles all show localised patterns of magnetic response. Neutral D_{3h} borazine, neutral D_{4h} borazocine and the borazocine dianion occupy local minima on the potential energy surface and for them the constraint is irrelevant. All other systems, neutral or charged, exhibit two or more vibrations of imaginary frequency in the planar geometry. Structural information is listed in the ESI. In all converged cases, the neutral, cation and anionic cyclic systems (under planar constraints, as necessary) are equilateral. In what follows, the calculated bond lengths of particular interest will be those in neutral $B_4N_4H_8$ (R(BN) = 1.431 Å) and dianionic $B_4N_4H_8{}^{2-}$ (R(BN) = 1.452 Å).

Adjustment of electron count to realise an "aromatic" number of π electrons in a charged monocycle requires

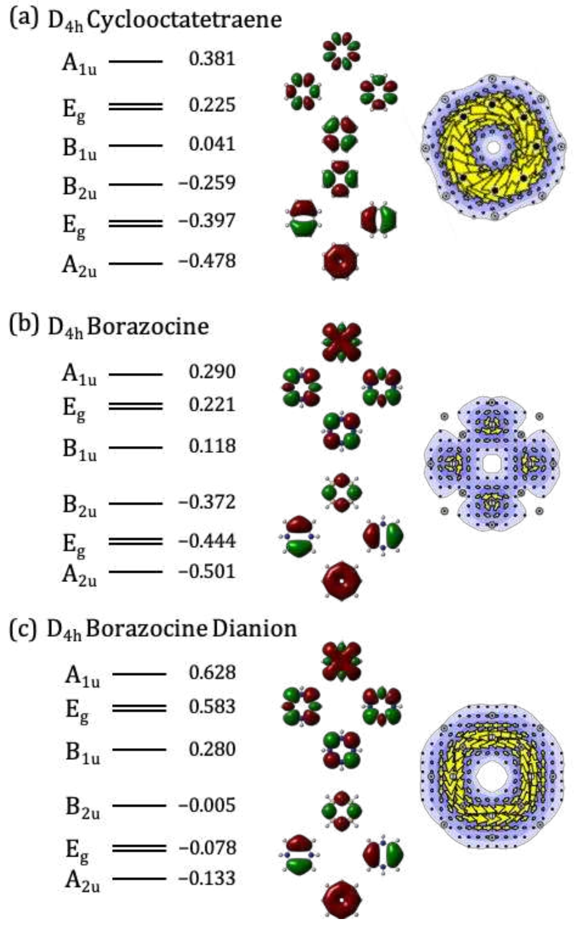

Figure 3: Energy-level diagram and π-current maps for (a) COT , (b) borazocine, and (c) D_{4h} borazocine dianion ($(BN)_4H_8{}^{2-}$), Schematic orbital-energy diagram highlighting the allowed frontier π-π* orbital excitations, and π-current density maps are shown in the left and right columns, respectively. CMO energies are given in E_h, orbital nodal patterns are shown on the right of the diagram, assignments to irreducible representations on the left. Orbital energies in a.u. are taken from DFT calculations at the planar geometries.

addition/removal of electrons to/from frontier π orbitals (2π electrons for even n and 4π electrons for odd n). With the exception of the D_{3h} borazine tetracation and tetraanion ($(BN)_3H_6^{\pm4}$), all charged D_{nh} $(BN)_nH_{2n}^q$ heterocyclic systems with the specified aromatic π electron counts show unambiguous aromaticity, with clear delocalised diatropic currents of a strength comparable to that in benzene (Figure 2). For example, j_{max} for the borazocine dianion is ~2.5 times the benzene standard value. Charged borazines are exceptional in that their calculations did not converge to D_{3h} ground states with the required number of π electrons. It proved impossible to force the added electrons of the anion or the holes of the cation to remain in the π/π* manifold. Attempted optimisation of the charged borazines results in the breaking of bonds between some or all hydrogen and boron centres or between hydrogen and nitrogen centres, in cation and anion, respectively. The origin of this tendency may lie in the stability of the conjugated π lone-pair system of the neutral molecule, with its large HOMO-LUMO gap acting as a barrier to departure from the 6π count in the ions.

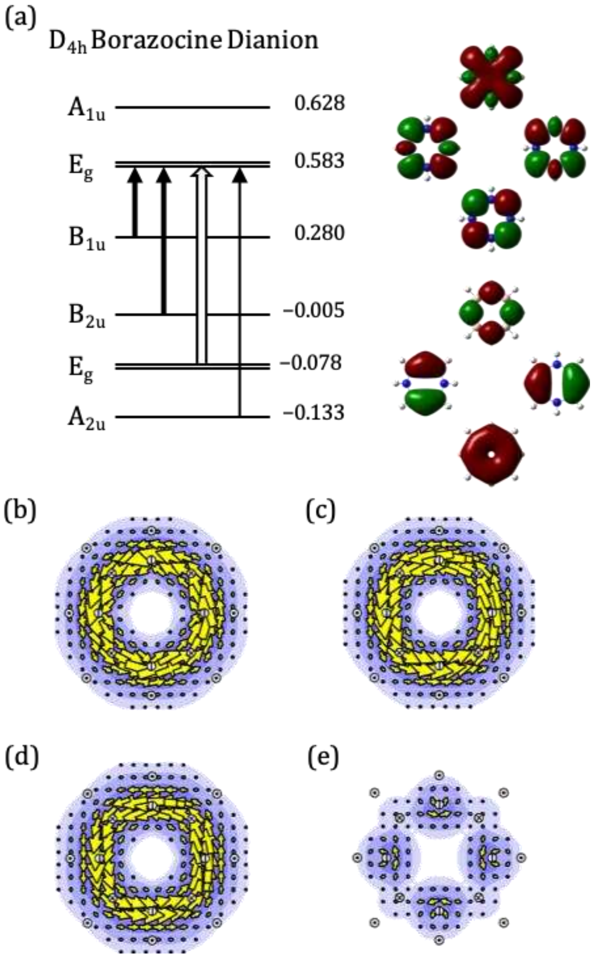

Figure 4: (a) Molecular-orbital analysis of the π-current in aromatic D_{4h} borazocine dianion, (b) the total 10π current (c) contributions to the total π-current arising from all possible transitions originating in the b_{1u}/b_{2u} $\Lambda = 2$ HOMO pair (d) combined contributions to total π current arising from the four possible transitions between the b_{1u}/b_{2u} $\Lambda = 2$ HOMO pair and the e_g $\Lambda = 3$ LUMO pair (e) the current contributions of the π orbital complement of the HOMO pair, i.e., map (b) minus map (c). Plotting conventions are described in the text. Full and hollow arrows indicate respectively translationally and rotationally allowed excitations in this symmetry group. Dominant contributions to current, determined by examination of maps of individual occupied-to-virtual orbital transitions,[88] are shown in bold.

The general picture bears out the expectation from Hückel theory that it should be possible to aromatise BN-heterocycles by manipulating total charge and π occupancy. As an example of the success of this approach, the addition of two electrons to neutral D_{4h} borazocine to produce D_{4h} borazocine dianion, both of which are predicted to be planar at this level of theory, is now examined in more detail.

Addition of electrons causes no significant change to the topology or nodal character of the frontier π orbitals of borazocine (see Figure 3(a)) in comparison with those of neutral D_{4h} borazocine (Figure 3(b)), or even when compared to those of the neutral [8]annulene, D_{4h} cyclooctatetraene (Figure 3(c)). All π manifolds retain the ordering by nodal count that originates in the classification of π orbitals of [n]annulene according to their angular momentum about the principle rotational axis, which is crucial to the rationalisation of the magnetic responses in the three different cases (Figure 3(a-c)). Orbitals with the same node count share a pseudo- quantum number, Λ, in terms of which selection rules can be written that determine whether a given virtual transition is diatropic or paratropic or both.[16,17]

Specifics of the π magnetic response depend both on the energy level diagram and the orbital occupancies. In COT the dominant orbital contribution to π ring current arises from the HOMO-LUMO transition across the split Λ = 2 pair, which is rotationally allowed, and hence gives a *paratropic* ring current. This current is partially cancelled by the diatropic contribution from the translationally allowed (HOMO-1)-LUMO transition (Λ = 1 to Λ = 2).

In neutral borazocine, the opening of the HOMO-LUMO gap leads to stronger cancellation with the net effect that the π currents localise on the nitrogen centres. (The outer and inner half-loops of a closed diatropic circulation around a nitrogen centre would appear to be diatropic and paratropic, respectively, when referred to the ring centre.)

In the 10π borazocine dianion, the Λ = 2, b_{1u}/b_{2u} split pair, which was HOMO+LUMO in the neutral becomes the new 'HOMO'. In this case, the dominant contribution to the ring current arises from the four translationally allowed Λ = 2 to Λ = 3 transitions from the new HOMO to the new LUMO pair, and hence is diatropic. Figure 4 (a-e) shows the detailed rationalisation of the dianion map, which turns out to be essentially the same as for the neutral planar 10π annulene.[16,17,20] The figure shows maps of total π current for the dianion, the HOMO contribution to that current, the summed contributions of the four transitions and the complement (obtained by spectral analysis of individual occupied to virtual orbital transitions).[16,34] It shows that the calculated total π-current is accounted for in all essential points by HOMO-LUMO virtual excitations.

On the magnetic criterion, the ability of a system such as borazocine dianion to sustain a diatropic π ring current is already definitive evidence of aromaticity, but it is also of interest to consider other, chemical, indications of aromatic behaviour. Aromatic moieties such as benzene and cyclopentadienide participate in sandwich compounds with

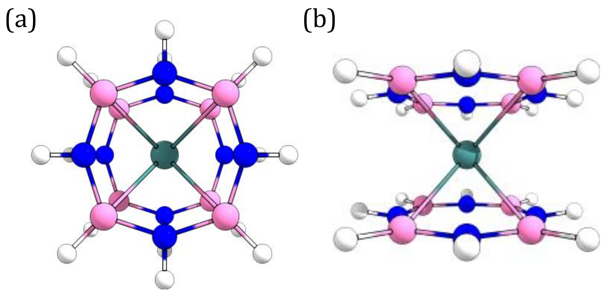

Figure 5: Minimum-energy structure of the $(B_4N_4H_8)_2Ti$ sandwich complex, top view (a) and side view (b).

transition metals, such as *bis*benzenechromium and ferrocene.[35] *Ab initio* explorations indicate that the borazocine dianion shares this tendency. According to optimisations carried out at the MP2/6-31G** level, the D_{4h} $(B_4N_4H_8)_2Ti$ sandwich structure occupies a local minimum on the potential energy surface, with near-planar azaboracycles in which N eclipses N, and B eclipses B, see Figure 5. The B and N atoms deviate by only ±0.02 Å from the medium plane of the heavy atoms in each borazocine moiety, with B lying closer to the central Ti atom. The calculated BN bond length, of R(BN)= 1.442 Å, lies halfway between the values for the neutral and dianionic borazocines, suggesting retention of aromaticity in the complex. Bond length changes of similar magnitude are found on complexation of benzene to chromium, for example.[36] In the *bis*borazocinetitanium complex, the vibrational mode of the lowest frequency describes in-plane shuttling of the metal ion between stations of NN pairs, and nearby modes correspond to ring tipping (see ESI for calculated frequencies). This structure gives additional evidence of aromatic nature of this appropriately charged azaboracycle.

In summary, the same π manifold of an eight-membered ring with different electron counts and η values has given rise to an aromatic, a non-aromatic and an anti-aromatic species - all with textbook characteristic patterns of ring current. As the planar D_{4h} borazocine dianion occupies a local minimum on the potential energy surface, this system is the most plausible candidate for an inorganic aromat, in this case the “inorganic cyclooctatetraenide anion” rather than the long-awaited “inorganic benzene”.

Conclusions

A strategy for predicting aromatic systems based on azabora rings with modified electron count has been used to detect ring-current aromaticity in the dianion of borazocine. This [8]azabora-annulene appears to represent an ideal ring size for our purpose, in that it has a planar equilibrium geometry and is able to accommodate additional π electrons. It has the magnetic response expected of an aromatic system.

However, and with hindsight perhaps predictably, the pure monocycle strategy did not produce an aromatised borazine. Calculations for the charged borazine monocycles proved impossible to converge with the specified π occupancy. Nor did experiments with clamping strategies, previously shown to exhibit global currents in systems such as COT, give global currents for the charged borazine. In previous calculations on all-carbon structures, when clamping groups were such as to leave the electronic structure at the HOMO-LUMO frontier intact, a central benzene/COT moiety was found to sustain a diatropic/paratropic ring current. If on the other hand the clamping groups used were such as to disrupt this frontier electronic structure, the central ring was always found to support localised π currents only.[37]

For clamped charged azabora-annulenes displaying a ring current in a given charge state, similar propensity rules might be expected to apply. In our exploratory calculations, however, clamping of borazine ions with saturated groups always gave retention of the 6π configuration of borazine, with excess charge affecting the σ occupancies only. An aromatised borazine, in which the π electrons have been coaxed into global circulation, therefore remains a tantalising prospect.

As one referee of this paper remarked, the observation that electronic and magnetic properties of azabora-annulenic systems can be tuned via charge doping may also be useful for design of molecular devices, where coupling to leads may also stabilise some of the structures that are predicted to be unstable as isolated species.

A further direction that has not been explored here, is the link between ring-current aromaticity and delocalisation of electrons in the unperturbed molecule. In the ipsocentric picture, ring currents arise from virtual transitions between molecular orbitals linked appropriately by the selection rules; in this picture, electron delocalisation is a *necessary* but not *sufficient* condition for ring-current aromaticity. Simple delocalisation indices such as the six-centre index have been shown to correlate with ring current patterns in benzenoids[38] as have more sophisticated indices.[39] Extension of such correlations for aromatised systems could be of interest.

Acknowledgements

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