

Aromaticity of Organic Heterocyclothiazenes and Analogues

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Abstract: Members of a series of carbon-poor sulfur–nitrogen heterocycles and polycycles are shown by direct ab initio ipsocentric calculation to support diatropic ring currents and hence to be aromatic on the basis of magnetic criteria. They include 7-cycles $S_3N_2(CH)_2$ (**1**), $S_3N_3(CH)$ (**2**), and S_3N_4 (**3**) and 8-cycles $S_2N_4(CH)_2$ (**7**) and $S_2N_2(CH)_4$ (**8**), all with 10 π electrons. The unknown trithiatetrazepine S_3N_4 is predicted to be at least as aromatic as its known diaza and triaza homologues. Angular-momentum arguments show that the π -electron-rich nature of $(4n + 2)$ SN heterocycles is the key to their diatropic current. The Woodward dithiatetrazocine parent framework $S_2N_4(CH)_2$ (**7**) supports a diatropic ring current, as does its analogue in which N and CH groups are formally exchanged. Formal expansion of $(4n + 2)$ - π carbocyclic systems by insertion of NSN motifs in every CC bond is predicted to lead to structures that support diatropic ring currents: explicit ab initio calculation of magnetic response predicts the 24-center, 30- π -electron heterocycle $S_6N_{12}(CH)_6$, formally derived from benzene, to be aromatic on the basis of this criterion.

Introduction

This study deals with a family of molecules lying at the borderline of organic (heterocyclic) and inorganic (sulfur–nitrogen) chemistry, cyclic and bicyclic systems with a high ratio of heteroatoms (S, N) to carbon (Chart 1). Several, including parent compounds trithiadiazepine (**1**),¹ trithiatetrazepine (**2**),² benzotrithiadiazepine¹ (**15**), and tetrathiatetraazulene (**16**),³ have been prepared and show classical indications of aromaticity.^{1–5} Such a match between carbocycles and formally π -isoelectronic heterocycles is not automatic, as the example of borazine shows.⁶ However, for many of these carbon-poor sulfur–nitrogen heterocycles, it does appear that the annulene analogy is a good one; the reasons for this success will be discussed below. Modern electronic structure theory offers a new tool for the scrutiny of aromaticity, through the induced current density and associated magnetic properties. This approach is used here to test the annulene analogy for species such as **1** and **2**, to reinvestigate some proposals for extension of this series of compounds, and to make further predictions for the design of aromatic systems.

A widely used criterion for aromaticity is based on ring currents: an aromatic system is one that supports a global diatropic ring current, an antiaromatic system one that supports a paratropic ring current.^{7–9} A direct way to investigate

aromaticity theoretically is therefore to calculate the current density induced in a planar molecule by a perpendicular magnetic field; this can nowadays be done efficiently and accurately using the *ipsocentric* method whereby magnetic response is calculated with a distributed origin, taking each point in turn as the origin of vector potential.^{10–12} This method delivers accurate maps of current density and allows partition of molecular currents into well-defined orbital contributions.¹² It has been applied to the mapping of currents in inorganic¹³ as well as many organic monocycles.

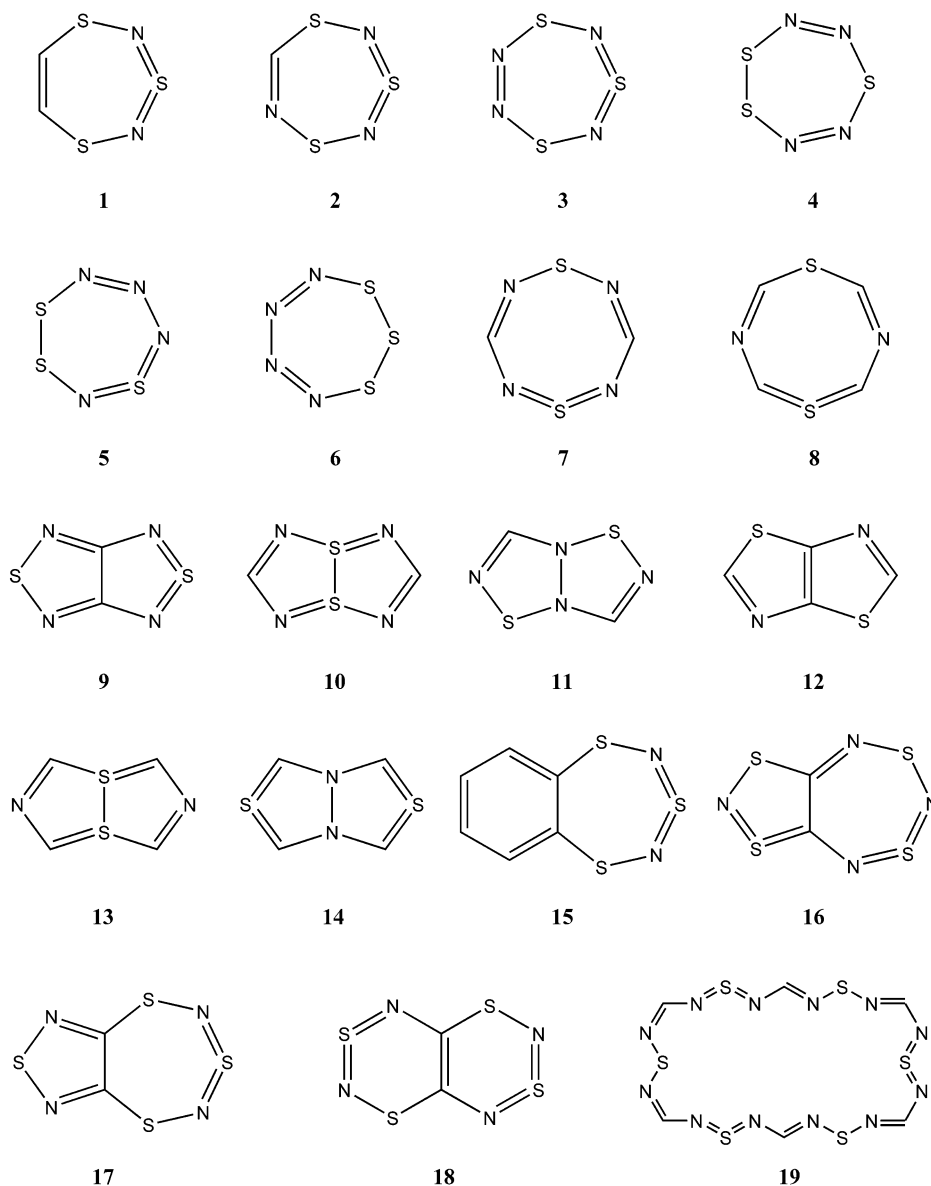
The expectation from the *ipsocentric* model is that a $(4n + 2)$ - π aromatic cycle will give a diatropic ring current that can be attributed almost entirely to response of the four most energetic π electrons. Conversely, an antiaromatic $4n$ - π cycle will give a paratropic ring current that can be attributed mainly to its two most energetic π electrons.¹⁴ These rules derive from an angular-momentum selection rule: in the *ipsocentric* model, currents arise from virtual transitions between occupied and unoccupied molecular orbitals of the cycle, paratropic where the transition is between orbitals with an equal number of angular nodes, diatropic where the transition increases this number by one. Application of the rules allows us to understand the results of calculations on the heterocyclic molecules, as presented below.

[†] University of Exeter.[‡] Imperial College.

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Chart 1. Molecular Systems Discussed in This Paper



Current-Density Calculations

All molecular structures in Chart 1 were optimized at the RHF and DFT (B3LYP) levels in the 6-31G** basis set, known to be sufficient for semiquantitative calculation of current-density maps.¹² Molecules **1–3**, **7–9**, **12**, **16**, **18**, and **19** are predicted at both RHF and DFT levels to have planar equilibrium geometries, whereas **15** and **17** have nonplanar geometries at the RHF level but return to planarity at the DFT level of theory. The other systems of Chart 1 (**4–6**, **10**, **11**, **13**, **14**) are all found to be nonplanar at both RHF and DFT levels. All planar optima show sets of bond lengths intermediate between those of formal single and double bonds (see Figure 1 for details of **1–3**, **7**, and **8**), suggesting extensive cyclic π delocalization. In all planar cases the HOMO and HOMO–1 are found to be of π character, and LUMO and LUMO+1 or LUMO+2 to be of π^* character.

Maps of the current density induced in the planar structures for molecules within the set by a perpendicular magnetic field, as calculated at the RHF optimum geometries within the coupled

Hartree–Fock (CHF) ipsocentric approach,¹⁵ are shown in Figures 3–5 and 7–9. The results for current density are now discussed, case by case. For comparison, the π ring currents of benzene and naphthalene computed in the same approach are shown in Figure 2. The arrows indicate the projection of current density in the plotting plane, $1a_0$ above that of the nuclei. Anticlockwise circulation of arrows indicates diatropic current. Maps of the CHF current density at DFT geometries are very similar in appearance, though with slightly larger currents. Each figure typically shows canonical molecular-orbital contributions to the induced current density from (a) HOMO–1, (b) HOMO, (c) the combined (HOMO–1, HOMO) pair, and (d) the full set of orbitals of π symmetry. For the larger systems (see (ii) to (v)), only full π current-density maps are given.

(i) **S₃N₂(CH)₂ (1)**, **S₃N₃(CH) (2)**, and **S₃N₄ (3)**: **10 π Electrons on Seven Centers.** 1,3,5,2,4-Trithiadiazepine (**1**) is a 10- π -electron system, prepared as volatile but thermally stable,

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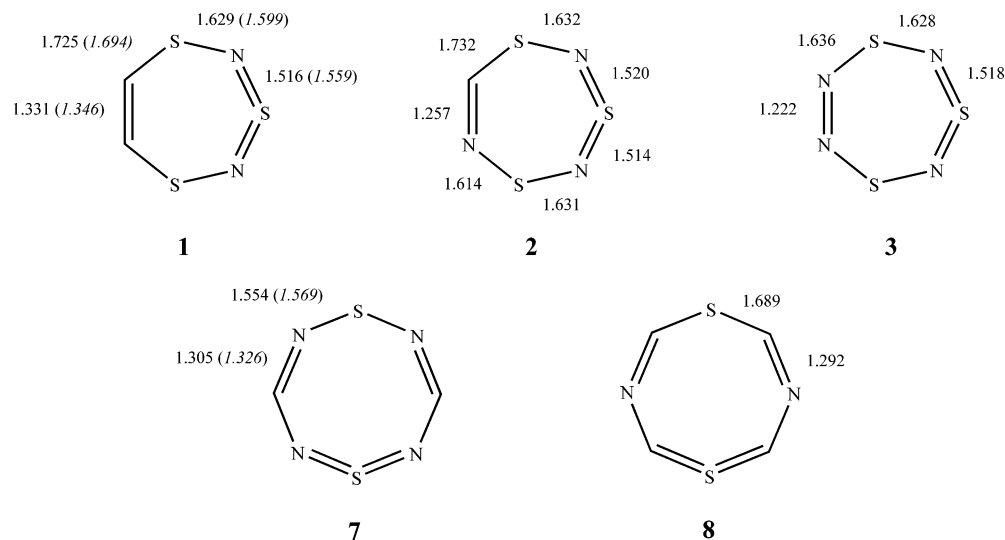


Figure 1. Bond lengths (Å) computed at the RHF//6-31G** level for molecules **1–3**, **7**, and **8**. Lengths determined by X-ray diffraction^{15,19} are given in parentheses; for **7** the experimental bond lengths refer to a derivative, where *tert*-butyl groups replace the two hydrogen atoms of the parent structure.

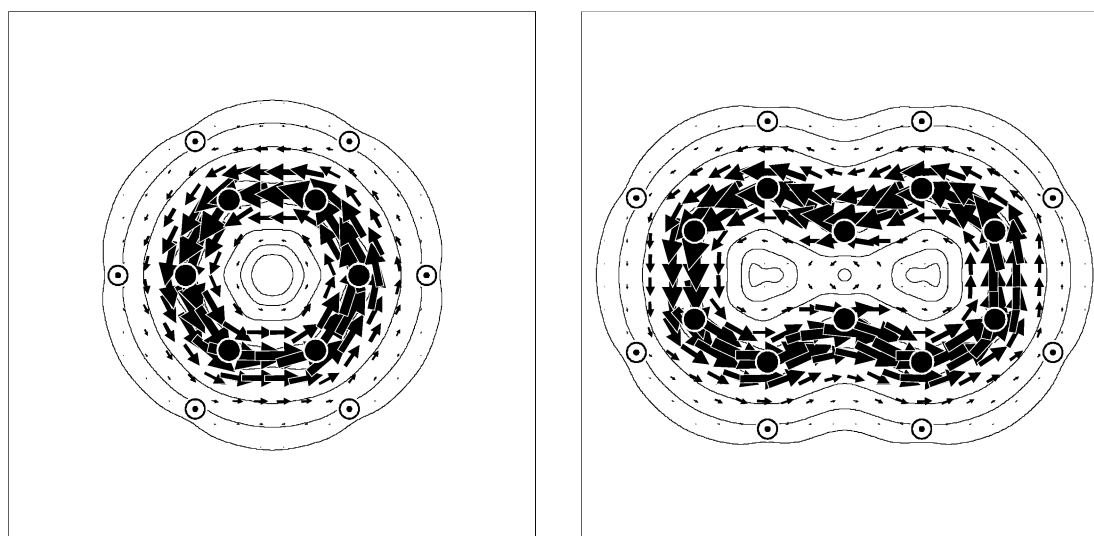


Figure 2. Typical aromatic ring currents arising from the set of π orbitals of benzene (left) and naphthalene (right). Current is plotted in the plane $1a_0$ above that of the nuclei. C and H centers are represented by filled and dotted circles, respectively.

colorless crystals from bis(sulfenyl chlorides) and bis(trimethylsilyl)sulfurdiimide.¹ Its planar geometry with intermediate bond lengths (Figure 1), as determined by X-ray diffraction, its chemistry, and its spectroscopy indicate aromaticity. The π -isoelectronic triaza species 1,3,5,2,4,6-trithiatriazepine (**2**) is also obtained as highly volatile, colorless crystals, with IR, UV, and NMR spectra similar to those of **1**, and showing decreased susceptibility to electrophilic attack.² An X-ray structure is not available for this compound, but previous calculations² as well as those reported here predict planarity. It has been proposed² that the series **1**, **2** could be continued to the carbon-free trithiatetrazepine (**3**). Compound **3** has not been prepared, nor has it been observed as a byproduct in any of the extensive series of reactions of S_4N_4 , but it is predicted to lie in a local minimum on the potential surface. Previous MNDO calculations on **3**² predict planarity, as do the present RHF and DFT optimizations. A possible mode of decomposition for the S_3N_4 ring would be by extrusion of neighboring N atoms as dinitrogen, although existence of a barrier to this process is guaranteed by the local-minimum character of **3**.²

Figures 3–5 show the π current-density maps for the molecules **1–3**, formally related by successive replacement of CH by N. As the maps of total π current density (panel d in each figure) show, all three systems are predicted to sustain marked diatropic ring currents originating in the π system, similar in appearance to the archetypal ring current in benzene (Figure 2). This circulation is reinforced by the σ electrons. All three molecules are therefore aromatic according to the magnetic criterion. In the plotting plane, the maximum π current density per unit inducing field is 0.084, 0.085, 0.094 au (RHF geometry) or 0.095, 0.095, 0.103 au (DFT geometry), to be compared with the equivalent value of 0.079 au for benzene. On the basis of raw current values, it is plausible to argue that **1**, **2**, and **3** are all at least “as aromatic” as benzene; after normalizing for ring area, all three systems still have 70–80% of the benzene area-reduced ring current.

Furthermore, the orbital contributions to the π ring currents are in accord with the paradigm for aromatic ($4n + 2$)-carbocycles. Partial contributions from HOMO and HOMO–1 (panels a and b in each figure) combine to give the global,

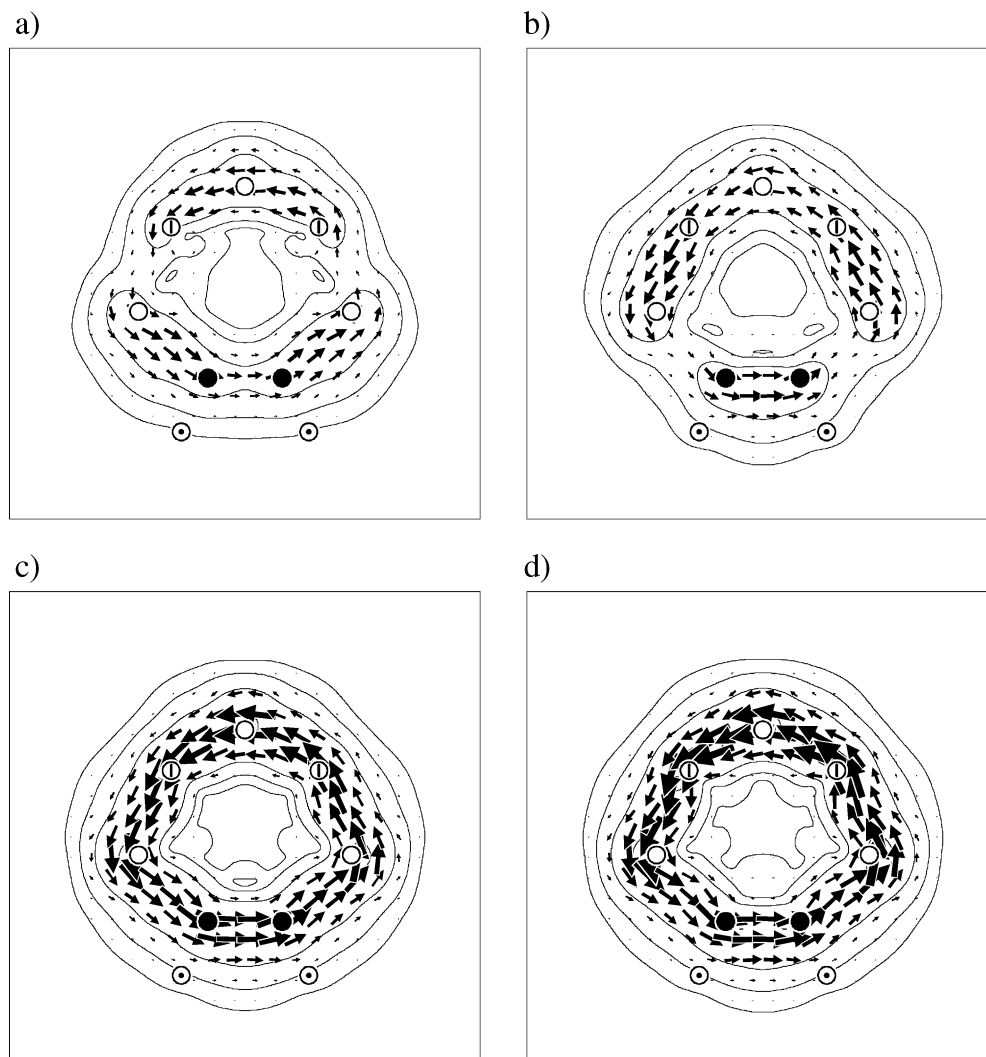


Figure 3. Canonical-molecular-orbital contributions to the induced current density in **1** arising from (a) the HOMO–1, (b) the HOMO, (c) the combined (HOMO–1, HOMO) pair, and (d) the full set of orbitals of π symmetry. Current is plotted in the plane $1a_0$ above that of the nuclei. C, S, N, and H centers are represented by filled, empty, barred, and dotted circles, respectively.

diatropic 4-electron ring current (c), essentially indistinguishable from the total π current (d). Domination of π current by two frontier orbitals follows from the *ipsocentric* description. Although split in symmetry, the (HOMO–1)/HOMO orbitals of **1–3**, each with two angular nodes, correspond to a pair of orbitals of angular momentum $\lambda = 2$ in the formal parent [7]-annulene. Likewise, LUMO/(LUMO+1) correspond to $\lambda = 3$ (see Figure 6). The node-increasing (and therefore diatropic) virtual transition from (HOMO/(HOMO–1)) to (LUMO/(LUMO+1)) makes a large contribution, which in the annulene parent would constitute the total π current.¹⁴ In the lower symmetry of **1–3**, angular-momentum mixing brings in further small contributions, but the topology of the contributing orbitals stays unchanged and the $\Delta\lambda = +1$ transition characteristic of the $(4n + 2)\text{-}\pi$ systems remains dominant.

As **3** has not yet been synthesized, it is of some interest to set it in the context of other possible isomers. A 7-cycle S_3N_4 has four possible constitutional isomers, which can be characterized in terms of the connectivity of the N atoms: the ring may contain one (**3**) or two N_2 chains (**4**), one N_3 chain (**5**), or one N_4 chain (**6**). Optimizations at the RHF/6-31G** level for **4** and **5** yield nonplanar structures, and no stationary point is

identified for **6**; only isomer **3** of S_3N_4 has the planarity associated with aromatic stabilization.

(ii) $S_2N_4(CH)_2$ (7**) and $S_2N_2(CH)_4$ (**8**): 10π Monocycles on Eight Centers.** There are only a few examples of carbon-poor SN monocycles characterized by 10π electrons on eight centers, and they are all derivatives of 1,5-dithia-2,4,6,8-tetrazocine (**7**). Woodward and co-workers¹⁶ prepared the first derivatives of **7** during an attempt to synthesize organic conductors through linear polymerization of sulfur diimide groups ($N=S=N$), π -excessive units characterized by four π electrons distributed over three centers. The reaction of benzamidine with sulfur dichloride in fact gave not the desired polymers, but a minor product of unusual properties: the 3,7-diphenyl-1,5-dithia-2,4,6,8-tetrazocine (the diphenyl derivative of **7**).

Many indicators of aromaticity were identified.¹⁶ X-ray diffraction showed the compound to be planar and geometrically delocalized. The UV spectrum showed a long-wavelength absorption band, assigned to a low-lying $\pi\text{-}\pi^*$ transition typical of aromatics. Furthermore, the Woodward group demonstrated an interesting property of these π -excessive compounds. A

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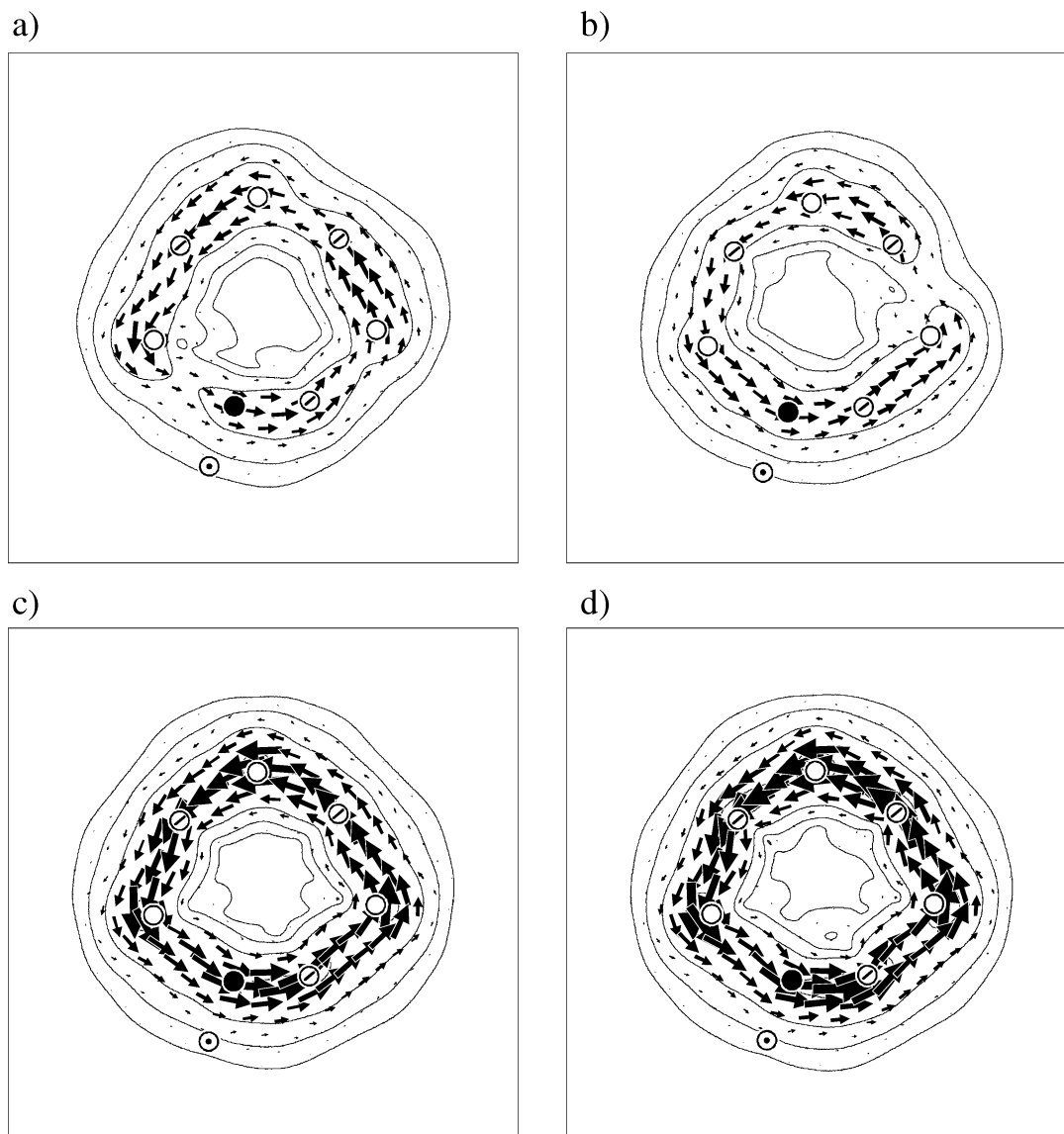


Figure 4. Canonical-molecular-orbital contributions to the induced current density in **2** arising from (a) the HOMO–1, (b) the HOMO, (c) the combined (HOMO–1, HOMO) pair, and (d) the full set of orbitals of π symmetry. Plotting conventions as in Figure 2.

delicate equilibrium seems to exist between the aromatic stabilization achieved in a π -delocalized planar structure, and competing structures involving formation of transannular bonds and departure from planarity. Synthesis of the 3,7-bis(dimethylamino) derivative of **7** yielded a nonplanar molecule, with an intense UV absorption band at a wavelength shorter than for a typical aromatic.¹⁶ π -Electron-donating substituents induced transannular S–S bond formation, leading to nonplanar bicyclic structures hinged on the S–S bond that retain eight of the original π electrons.

Several other 3,7-substituted dithiatetrazocines have been synthesized and characterized,^{17–19} but the parent compound **7**, to the best of our knowledge, has not been prepared. Reported MNDO and ab initio calculations using small basis sets¹⁷ support the hypothesis of planarity of **7**, and together with results from photoelectron spectroscopy reveal the π/π^* nature and symmetries of the frontier orbitals. These theoretical results receive

further support from geometry optimization at the RHF/6-31G** and B3LYP/6-31G** levels of theory: in both cases, a planar structure for **7** is a true local minimum (Figure 1).

Figure 7a shows the π current-density map computed for the RHF-optimized structure. The total π current is intense and diatropic, providing strong confirmation for the conjectured aromaticity of 1,5-dithia-2,4,6,8-tetrazocine. A check of the orbital contributions to the total π current showed that the π magnetic response is dominated by the quasi-degenerate pair HOMO/(HOMO–1), giving a ready rationalization for the origin of ring current in this aromatic monocycle. Both HOMO/(HOMO–1) and LUMO/(LUMO+1) pairs are characterized by precise nodal counts,¹⁷ corresponding to angular momentum $\lambda = 2$ and $\lambda = 3$, and hence in the *ipsocentric* orbital model lead to the purely diatropic orbital contributions that dominate the total π current density.

Although the 3,7-substituted derivatives of dithiatetrazocine are the only experimentally characterized representatives of the class of 10π monocycles on eight centers, it is useful to explore other possibilities. A simple formal transformation of **7** that

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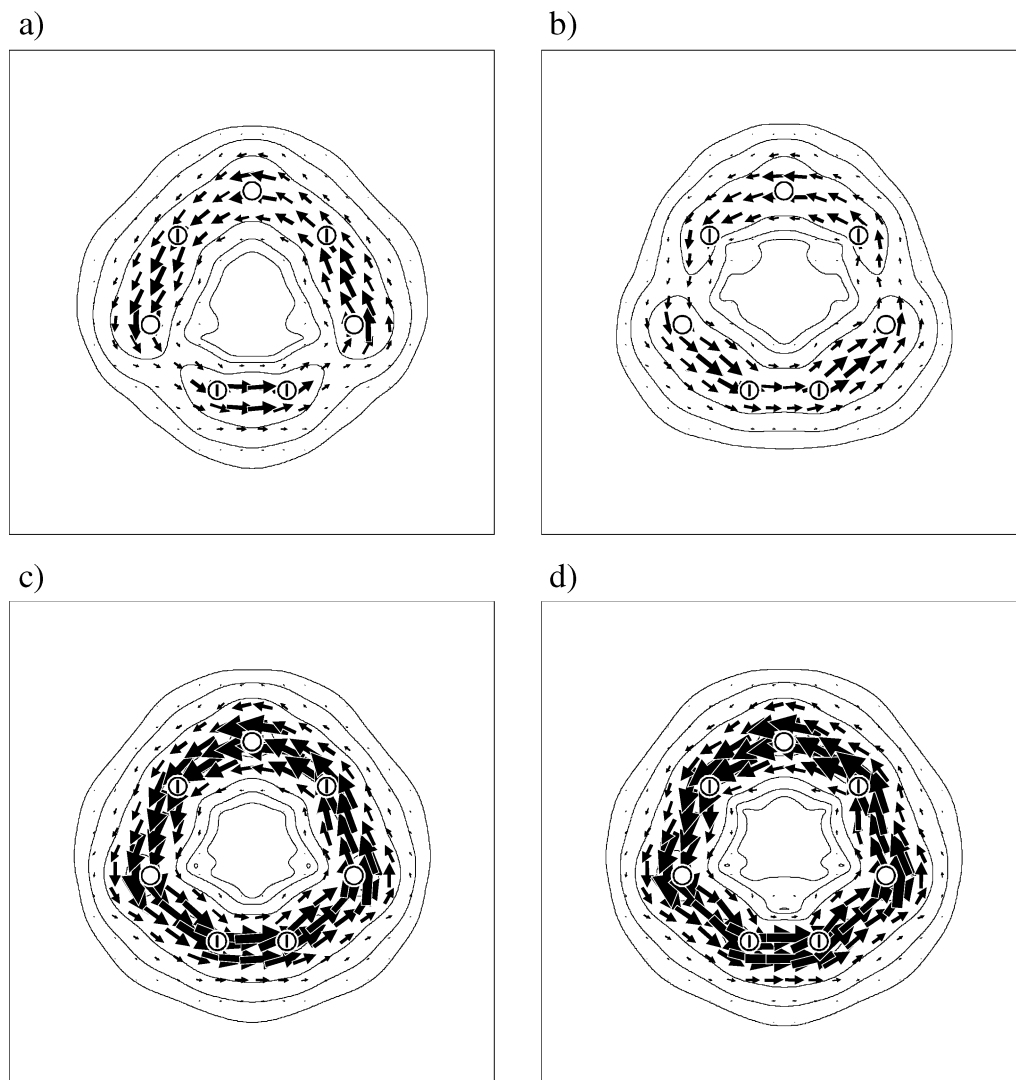


Figure 5. Canonical-molecular-orbital contributions to the induced current density in **3** arising from (a) the HOMO–1, (b) the HOMO, (c) the combined (HOMO–1, HOMO) pair, and (d) the full set of orbitals of π symmetry. Plotting conventions as in Figure 2.

leaves unchanged the number of π electrons donated by each center is realized by exchanging N and CH centers, to obtain a hypothetical structure of formula $S_2N_2(CH)_4$ (**8**).

Full optimization of **8** at both RHF/6-31G** and B3LYP/6-31G** levels of theory yields planar structures, characterized as true local minima (Figure 1). A π current-density map is shown in Figure 7b. The general features of the induced current density are the same as for **7**: the global diatropic induced ring current, and its origin in the four electrons of the quasi-degenerate HOMO/(HOMO–1) pair, are clear indicators of Hückel aromaticity for compound **8**. The lower intensity of the induced current density in the unknown system **8** suggests less pronounced π electron delocalization. The ability of the sulfur-diimide group to achieve better delocalization than the isoelectronic CSC group is a property that suggests further use of NSN building blocks (see (v) below).

(iii) $S_2N_4C_2$ (9**) and $S_2N_2C_4H_2$ (**17**): 10π Bicyclic Systems.**

One way to rationalize the magnetic properties of naphthalene is to regard it as a perturbation of [10]annulene, obtained by formal inclusion of a cross-link between antipodal carbons, followed by formal elimination of H+H. This transformation preserves π electron count and, most importantly, frontier orbital

topology, and therefore, according to the orbital model, the aromaticity of the parent annulene.²⁰ Naphthalene exhibits a typical π ring current flowing along the molecular perimeter (Figure 2).

To explore the series of 10π aromatics on eight centers, one can imagine applying the same formal procedure to all possible antipodal atom pairs of the monocycles **7** and **8**, to yield the series of bicyclic molecules **9–14** (Chart 1). As we have already seen, although transannular S–S bond formation represents a plausible process from a chemical point of view, it is likely to lead to nonplanar structures on withdrawal of two electrons from the π network, which will be antiaromatic on the annulene analogy and, therefore, unstable. Likewise, transannular N–N bond formation adds two to the formal π count. Geometry optimization of S–S bonded compounds **10** and **13** and N–N bonded **11** and **14** does indeed lead to nonplanar minima in all four cases.

Cross-linking of CH groups with hydrogen elimination does not change the π count, and the known^{21,22} molecules **9** and **12** in this series are characterized as planar bicyclic minima.

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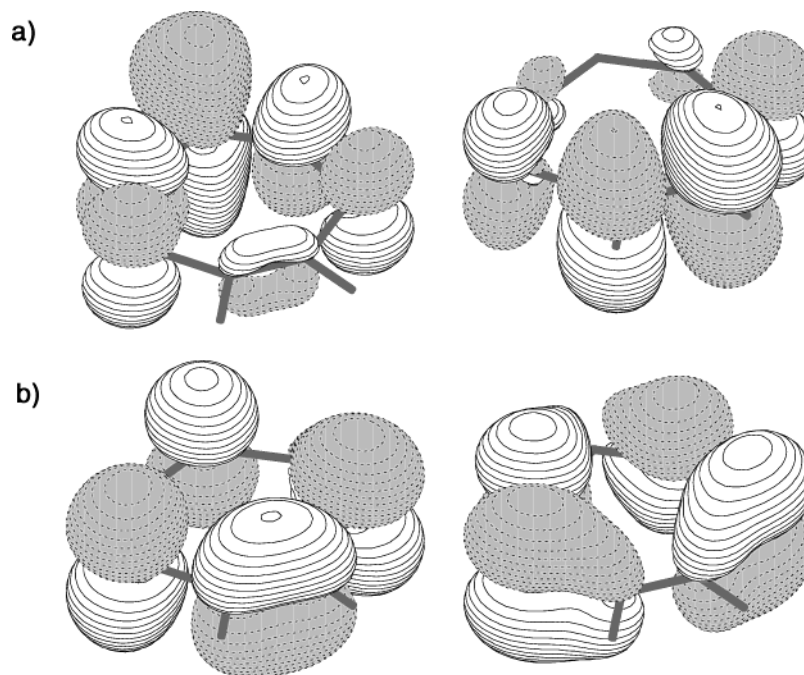


Figure 6. Frontier canonical orbitals of trithiadiazepine. (a) (HOMO–1)/HOMO pair (two angular nodes, angular momentum $\lambda = 2$), (b) LUMO/LUMO+1 pair (three nodes, $\lambda = 3$).

Comparison of the total π current-density maps for **9** and **12** (Figure 7c,d) shows significant differences, although both molecules would be classified as aromatic according to magnetic criteria. **9** exhibits a strong and uniform diatropic perimeter circulation, of comparable intensity to that of the parent monocycle **7**, and similar to that in naphthalene (Figure 2), whereas **12** displays a perimeter ring current considerably weaker than that of its parent compound **8**, and also much less uniform. In both molecules, the dominant orbital contributions to the total diatropic current are those of the four electrons occupying the nearly degenerate HOMO/(HOMO–1) pair, exactly as expected on the orbital model.

This trend in π -current strength and uniformity is in agreement with that for the parent monocycles, further underlying the key role played by NSN units in these delocalized heterocyclic compounds.

(iv) S₃N₂C₆H₄ (15) and S₄N₄C₂ (16): 14- π -Electron Bicyclic Systems. The benzo derivative of trithiadiazepine (**1**) by annelation across the C₂ bond, benzotrithiadiazepine (**15**), was prepared as a bright-yellow crystalline solid by reaction of benzene-1,2-bis(sulfonyl chloride) with bis(trimethylsilyl)sulfur diimide.¹ Its planar geometry, intermediate bond lengths (determined by X-ray diffraction²³), and spectroscopic characteristics were taken to indicate 14- π -electron aromaticity. Unexpectedly, tetrathiatetraza-azulene (**16**) was formed by reaction of tetrasulfur tetranitride and phenyl vinyl sulfoxide as a green-black crystalline solid with a metallic luster;³ X-ray diffraction showed the molecular structure to be planar, with SN bonds of similar length throughout, indicating delocalization

and again presumably 14- π -electron aromaticity. Two hypothetical structures,³ isomeric with (**16**), preserving the alternation of S and N centers are **17** and **18**, an “inside-out” analogue of the azulenoid (**16**) and an analogue of naphthalene.

Optimization of all four structures in the 6-31G** basis at the RHF level gave nonplanar geometries for **15** and **17** but planar geometries for **16** and **18**; reoptimization in the same basis at the B3LYP level gave planar geometries for all four systems. All four systems have the intermediate bond lengths expected of delocalized systems. Current-density maps were plotted at the planar RHF geometries for **16** and **18**, but at the DFT geometries for **15** and **17**. Figure 8 shows the π current-density maps for **15**–**18**. All four molecules exhibit diatropic perimeter circulations; these are more intense on the 6-cycle of **15** and the 5-cycle of **17**, but arise predominantly from the HOMO pair. **17** shows a significant current in the cross-link bond, whereas **18** has no cross-link π current, in close analogy with naphthalene (Figure 2), where such a current is forbidden by symmetry.²⁰ All four systems can reasonably be regarded as aromatic on the basis of the magnetic criterion.

(v) Expanded Monocycles: 30 π Electrons on 24 Centers, S₆N₁₂(CH)₆ (19). A systematic procedure to design neutral $[4n + 2]$ sulfur–nitrogen heterocycles without N–N or S–S bonds can easily be devised using “decoration” arguments considering a carbocycle as the starting point. Progressive formal insertion into every CC bond of N=S=N or N=CH–S units provides a way of introducing nitrogen and sulfur atoms so that an even number of π electrons is conserved. In particular, since both units are 4- π -electron donors, decoration of a $[4n + 2]$ carbocycle leads to a $[4m + 2]$ SN heterocycle, where, if k is the number of decorated bonds, $m = n + k$.

Examples of the procedure are **7** and **8**, where decoration of C=C, considered as a formal “[2]carbocycle” ($n = 0$), with N=S=N and N=CH–S, leads to two different 10- π -electron

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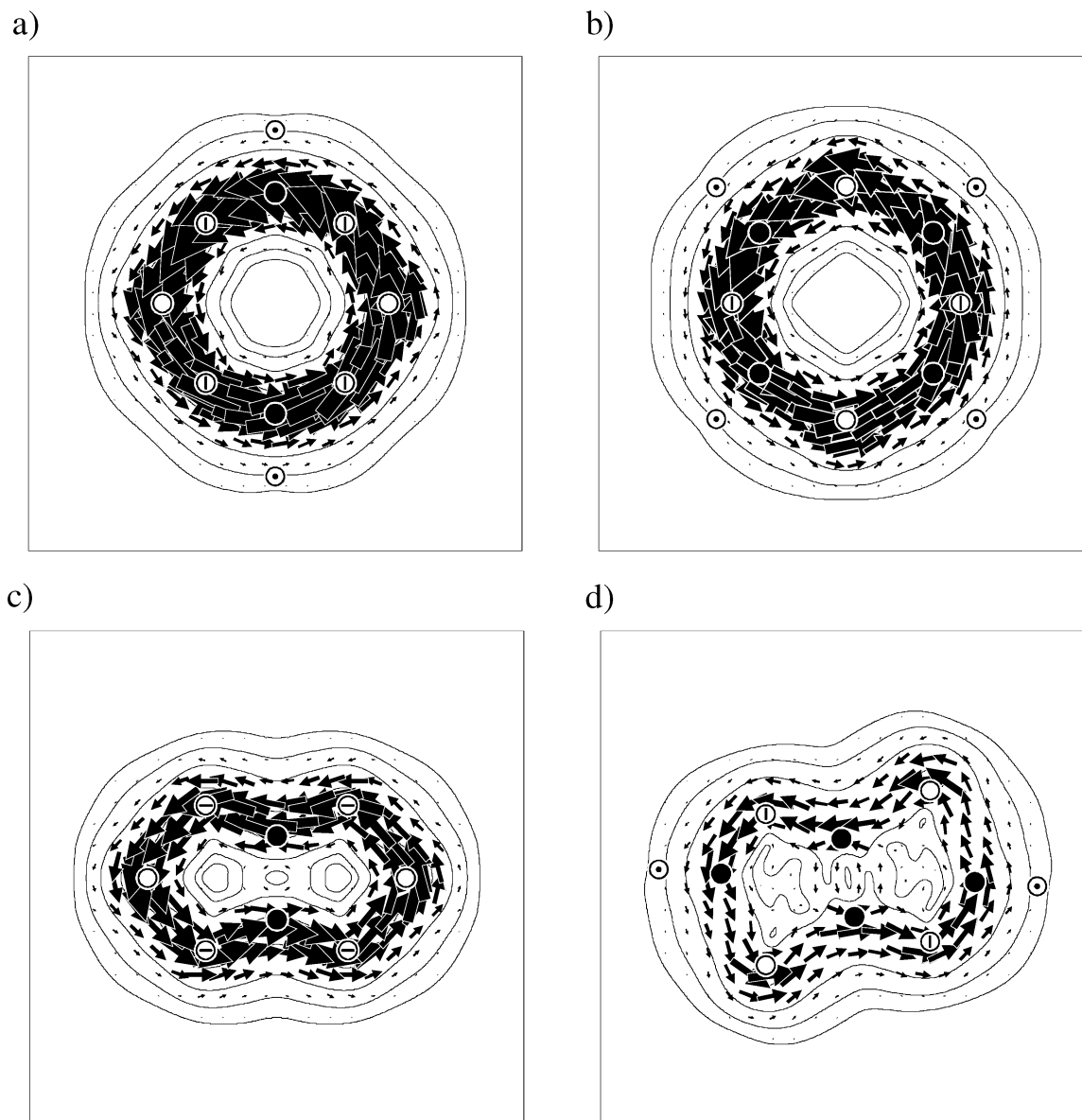


Figure 7. π -molecular-orbital contributions to the induced current density in two 10 π 8-cycles and two formally derived bicycles: (a) $S_2N_4(CH)_2$ (**7**), (b) $S_2N_2(CH)_4$ (**8**), (c) $S_2N_4C_2$ (**9**), and (d) $S_2N_2C_4H_2$ (**12**). Plotting conventions as in Figure 2.

systems. Contraction of opposite CH–CH units then gives a route to π -isoelectronic bicycles **9** and **12**. Chart 1 shows the next homologue in the first series, where the six CC bonds of benzene have been decorated by NSN 4- π -electron units, leading to a hypothetical 24-atom heterocycle with 30 π electrons (**19**). The planar structure of **19** occupies a local minimum and, as the map of π current (Figure 9) shows, is aromatic on the magnetic criterion. The diatropic π current calculated for **19** is ~ 3 times as strong as that in benzene, calculated by the same method in the same plotting plane.

The magnetic response of the expanded monocycles can be understood from the effect of NSN insertion on the orbitals and energies of the parent. Let α_N and α_S be the Coulomb integrals for N and S, defined as $\alpha_N = \alpha + \eta_N\beta$ and $\alpha_S = \alpha + \eta_S\beta$, where C would have $\eta_C = 0$. As sulfur and nitrogen are more electronegative than carbon, η_N and η_S are both positive; typical choices for 1- π N and 2- π S are $\eta_N = 1$ and $\eta_S = 0.5$.²⁴ Figure 10a shows the orbital energy levels calculated for **19** with these

parameters. The stack of levels for **19** has a quadruple structure that can be understood as follows.

The $16n + 8$ energies, $\mu = (\epsilon - \alpha)/\beta$, of the NSN-expanded graph can be derived from the $4n + 2$ energies, $\lambda = (\epsilon - \alpha)/\beta$, of the parent graph by finding the roots of the quartic equation:

$$\{(\mu - \eta_N)(\mu - \eta_C) - 2\}\{(\mu - \eta_N)(\mu - \eta_S) - 2\} - 2 - \lambda = 0$$

Each parent λ generates four energies μ in the expanded cycle, all of the same degeneracy as λ . Derivations of a number of similar results are given elsewhere.^{25,26} The expansion corresponds to repeated edge-subdivision of the carbocycle, first by

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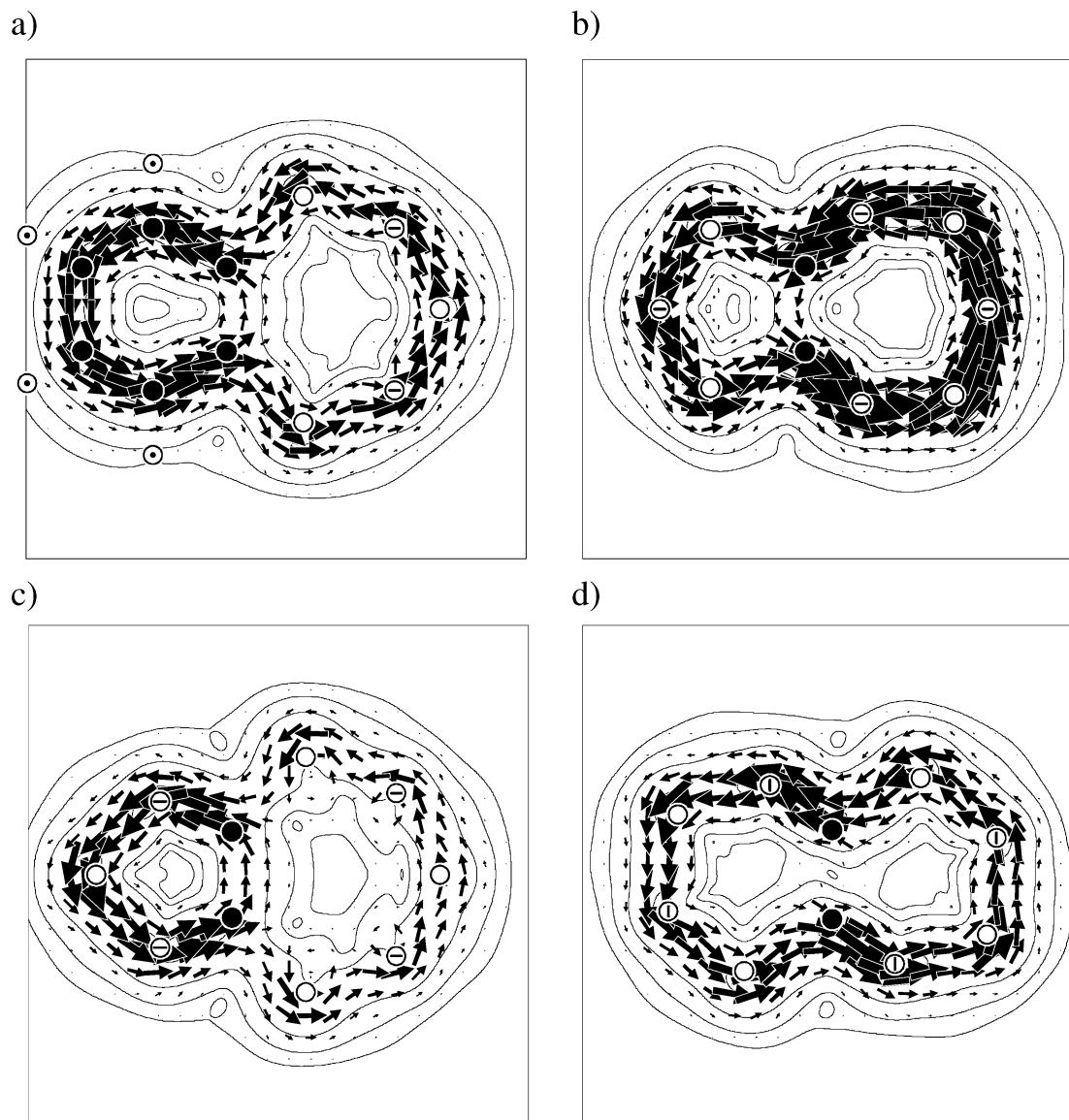


Figure 8. π -molecular-orbital contributions to the induced current density in four 14π bicycles. Systems **15–18** are shown in panels a–d, respectively, with plotting conventions as in Figure 2.

insertion of S on all edges, then by insertion of N (Figure 10b); each subdivision has well-characterized effects on orbital energies,²⁵ modulated here by the differences in electronegativities of inserted and original atoms.²⁶

For all plausible values of η_N and η_S , the energies of the expanded cycle (in this case **19**) span four copies of those of the parent (in this case, benzene), all compressed and two reversed, but each retaining a correspondence between the ordering of λ and μ (Figure 10b). The decoration process retains the $D_{(4n+2)h}$ symmetry of the parent graph, and hence the parity classification of MOs. Within each copy, g and u symmetries alternate, and the number of angular nodes increases steadily with energy. These conserved symmetry properties lead to a prediction for the magnetic response and aromaticity of the expanded heterocycle. The HOMO and LUMO of the expanded molecule occur at HOMO and LUMO positions of the third copy of the parent levels (see Figure 10a). Accordingly, HOMO and LUMO of the NSN heterocycle have exactly the same symmetries as those in the parent carbocycle, the two orbital

pairs having opposite parity and differing by one unit of angular momentum. In the ipsocentric orbital model, this latter condition is sufficient to render the dominant HOMO–LUMO transition purely diatropic, and hence for the class of expanded heterocycles to be considered aromatic on the magnetic criterion. As the full ab initio calculations bear out, this simple analysis has revealed the salient features of the ring-current response of **19**.

Conclusion

We have seen that a number of SN heterocycles are aromatic in the sense of supporting a diatropic ring current, and that in these aromatic systems the π electron count coincides with the predictions of the Hückel $4n + 2$ rule. In the particular case of NSN decoration, detailed arguments have clarified the orbital origin of the ring current and have shown that the $5(4n + 2)\text{-}\pi$ heterocycle is aromatic for the same symmetry reason as its $(4n + 2)\text{-}\pi$ parent. However, the general question posed in the

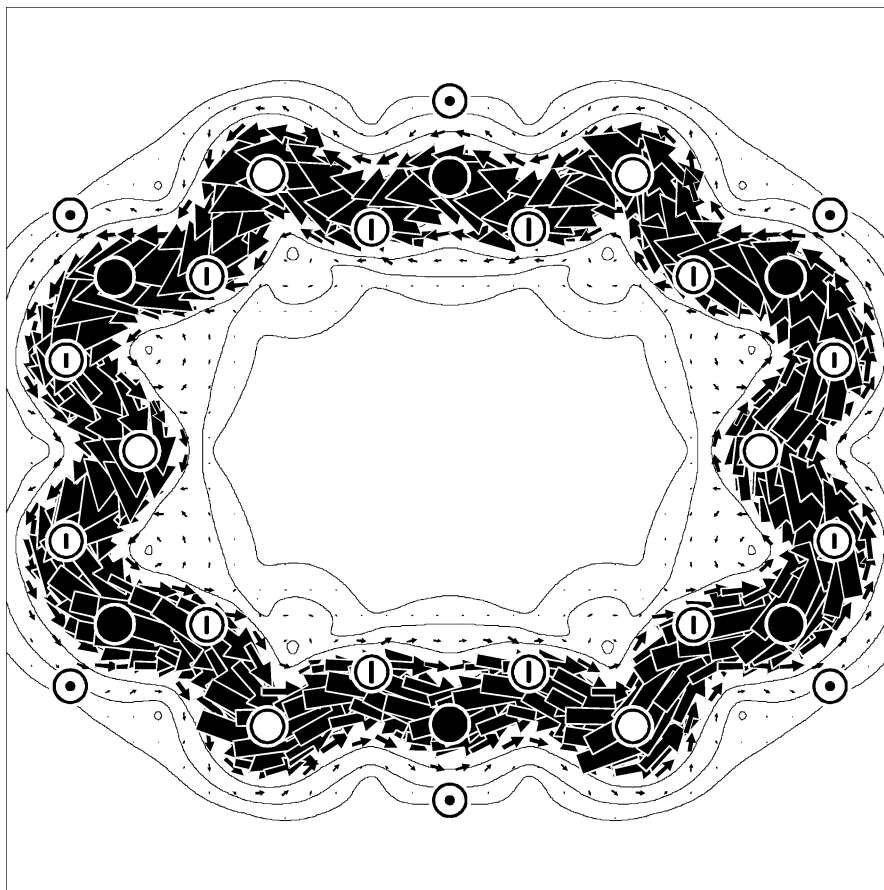


Figure 9. π -molecular-orbital contributions to the induced current density in a 24-center, 30π heterocycle $S_6N_{12}(CH)_6$, (**19**), formally derived by insertion of NSN units in the CC bonds of benzene. Plotting conventions as in Figure 2.

Introduction remains: Why is Hückel counting successful in predicting aromaticity for systems such as **1–3**, when it fails for other heterocyclic systems such as borazine? The low symmetry of many of the species militates against a clear-cut orbital analysis, but we can set up a plausible model based on Hückel theory which suggests the answer to the question.

SN heterocycles differ from carbocycles in two ways: in symmetry and in the π electron count for a given number of centers. Consider the two 6-cycles $B_3N_3H_6$ and $S_3N_3^-$. In simple Hückel theory, the π MOs of these D_{3h} molecules can be expressed as combinations of the standard D_{6h} symmetry-adapted orbitals. In the D_{6h} cycle, the six MOs occur in pairs with equal and opposite bonding and antibonding energies, and each orbital has a well-defined angular momentum value. When the symmetry group is halved to D_{3h} , every original bonding orbital is able to mix with its antibonding partner, and thus to combine two different angular momentum values. (Figure 11a illustrates the two cases, indicating orbital symmetry and angular momentum makeup in the different point groups.)

The consequences for ring current of this mixing depend crucially on the degree of filling of the π orbitals (Figure 11b). When the π system is *half full*, we have the analogue of the uncharged carbocycle. Borazine has six π electrons and no global π ring current.²⁷ At half-filling, HOMO and LUMO mix functions whose angular momentum originally differed by 1. This allows the originally diatropic HOMO–LUMO transition to gain paratropic character, tending to quench global ring

current. The degree of localization of induced current density depends on the electronegativity difference embodied in the Hückel α parameters. In $B_3N_3H_6$, localization is essentially complete.

Although sulfur and nitrogen are closer in electronegativity than nitrogen and boron, pure electronegativity arguments would suggest a significant loss of aromaticity. However, the other crucial property of SN heterocycles is that they are π -electron-rich. The direct structural analogue of borazine, $S_3N_3^-$, has been shown to sustain a strong diatropic ring current.¹³ $S_3N_3^-$ presents the same π -orbital sequence (A'' , E'' , E'' , A'') as borazine. In 6π borazine, HOMO and LUMO are of E'' symmetry and the HOMO–LUMO transition has therefore both $\Delta\lambda = 0$ and $\Delta\lambda = 1$ components. $S_3N_3^-$ has 10 π electrons, with E'' π HOMO and A'' π^* LUMO: A'' orbitals have mixed $\lambda = 0$ and $\lambda = 3$ character, and E'' orbitals have mixed $\lambda = 1$ and $\lambda = 2$ character (Figure 11a). Hence, the additional four π electrons of $S_3N_3^-$ lead to a HOMO–LUMO transition that has exclusively $\Delta\lambda = 1$ components, and thus to a pure diatropic current.

The crucial difference between half- and over-half-filling is that it is only when the HOMO–LUMO transition is between the central levels of the π energy-level diagram that this transition supports *both* paratropic and diatropic ring-current contributions (Figure 11b). At all π -electron-rich or π -electron-poor $4n + 2$ fillings, the current, if any, is purely diatropic. SN heterocycles therefore turn out to be perfect cases for naïve Hückel electron counting, despite their electronegativity alternation.

(27) Fowler, P. W.; Steiner, E. *J. Phys. Chem.* **1997**, *101*, 1409.

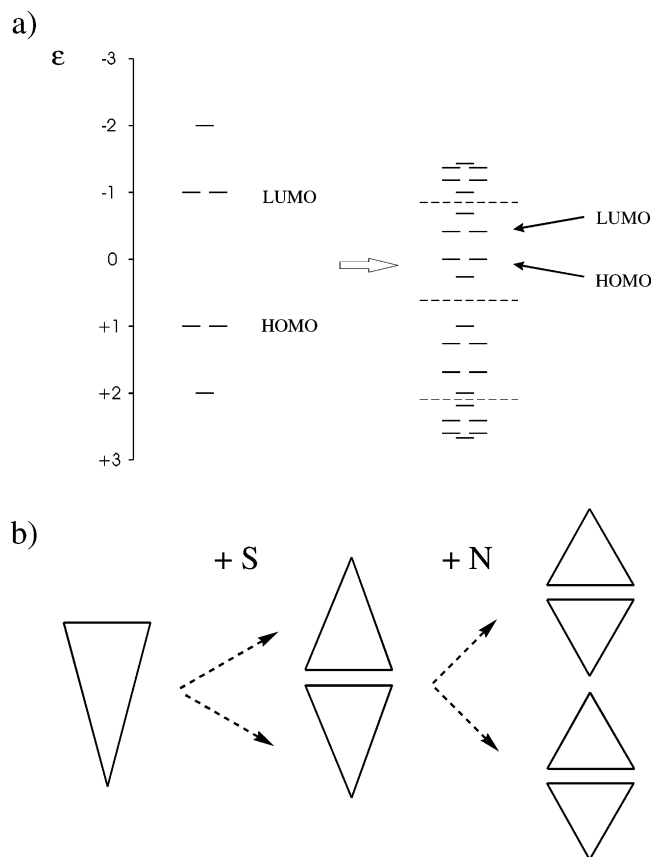


Figure 10. (a) Orbital energy level diagram for benzene (left) and the expanded heterocycle **19** (right). Orbital energies ϵ are plotted in units of β with an origin at α . The scale rises from positive (bonding) to negative (antibonding). HOMO and LUMO levels of both formally aromatic systems are indicated. Dotted lines show the grouping of the energies of **19** into four (distorted) copies of the energy level diagram of benzene. (b) Schematic description of the effect on the π energy levels of a cycle of insertion in a cycle of three vertices per edge, interpreted as two consecutive operations of insertion of one vertex per edge.²⁵ The schematic triangular motifs illustrate the compression (and inversion) of the original energy levels in the four copies.

A corollary is that if borazine could be charged with extra π electrons without destroying the planar structure, a ring current would appear for this molecule too. A test RHF/6-31G** ipsocentric calculation on the tetra-anion $B_3N_3H_6^{4-}$ constrained to a planar geometry (four imaginary frequencies) confirms this expectation: this hypothetical anionic system shows a diatropic π ring current similar in strength to the classic benzene current.

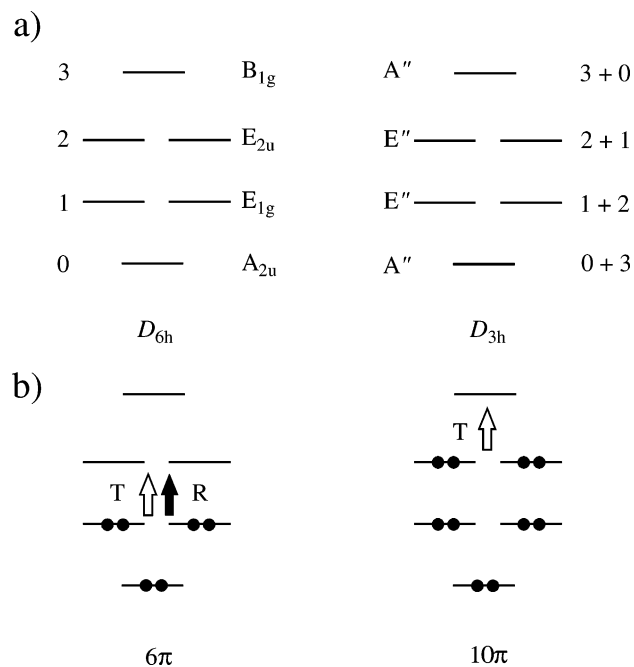


Figure 11. Effects of symmetry and orbital occupancy on π ring currents. (a) Schematic π -energy-level diagram for D_{6h} and D_{3h} six-membered rings, showing symmetry labels and contributing angular momentum components. Notation: 3+0 implies that the major contribution is from $\lambda = 3$, the minor contribution from $\lambda = 0$. (b) Consequences for the HOMO–LUMO transition at different fillings of the π shell in D_{3h} . At the 6π half-filling (left), the transition has both $\Delta\lambda = 0$ (Rotational, paratropic) and $\Delta\lambda = 1$ (Translational, diatropic) components. At the 10π filling (right), the transition has a $\Delta\lambda = 1$ but no $\Delta\lambda = 0$ component, and is translational (diatropic).

Addition of four electrons suffices to transform the current-density map of the neutral compound, and to convert borazine into an “aromatic”.

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Supporting Information Available: Atom coordinates for optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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