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ORIGINAL PAPER

Carbon–nitrogen nanorings and nanoribbons: a theoretical approach for altering the ground states of cyclacenes and polyacenes

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Abstract Carbon–nitrogen nanorings with formulae $(CN)_{2n}$ and in the form of [n]pyrazine cyclacenes appear either as closed-shell singlets (S_{CS}) for $n = 5$, 10, and 12, or open-shell singlets (S_{OS}) for $n = 6$, 7, 9, and 11 at restricted and unrestricted broken spin-symmetry density functional theory (DFT). All of their corresponding acyclic isomers, which are called [n]pyrazine polyacenes or nanoribbons, appear as S_{CS} for $n = 5$–12. As a result, nitrogen substitutions alter the electronic ground state of cyclacenes and polyacenes and appear to increase their viability, which invites further experimental and theoretical realization and exploration.

Keywords Cyclacenes · Polyacenes · Nanoring · Nanoribbon · Pyrazine

Introduction

Belt-shaped conjugated systems with radial orientation of p orbitals are geometrically regarded as attractive synthetic targets. Typical representatives of this family are [n]cyclacenes (**1**) as well as cyclo[n]phenacenes (**2**, $n = 10$) which are termed nanorings (Fig. 1) [1]. They are of interest for their possible utility as cylindrical cavities in host–guest chemistry and have the potential of serving as simple models for nanotubes [2]. Several attempts to synthesize [n]cyclacene (**1**) have failed [3–10]. Consequently, the current knowledge on [n]cyclacenes is contained in several density functional theory (DFT) and semiempirical investigations [11–18]. According to some computational studies, cyclacenes are predicted to possess triplet (ferromagnetic) ground states [2, 13–17]. In contrast, Chen et al. stated that "along with strain, the radical character of the open-shell singlet with antiferromagnetically (AFM) coupled electron spins may contribute to the difficulties in synthesizing [n]cyclacenes" [19]. They introduced [n]cyclacenes as the shortest four-layered (n,0) zigzag carbon nanotube models, and showed the AFM characters for the six-layered models. Very recently Sadowsky et al. [20] stated that modeling based on a combination of DFT and multiconfigurational wave function theories is indicative of an increase in diradical and eventually polyradical characters in [n]cyclacenes with increasing n. Consequently, this character also increases as the cyclacenes are extended to form finite-length (n,0) single-walled nanotubes.

As pointed out, the bending of a ribbon of annulated six-membered rings into a torus and the high intrinsic reactivity of larger cyclacenes are two main obstacles in the synthesis of these species. One approach to get around these is the incorporation of eight-membered rings as shown in structure **2** [21, 22]. The bending problem could also be avoided in different types of cyclacenes containing sulfur and nitrogen atoms which are predicted to be thermodynamically stable macrocycles [23].

On the other hand, polyacenes are acyclic variants of cyclacenes, which are viewed as zigzag-edged graphene nanoribbons (ZGNR) with a width index of two [24]. They have attracted wide interest from both theoretical and experimental scientists [25, 26]. For instance, pentacene has received much attention as an active semiconducting

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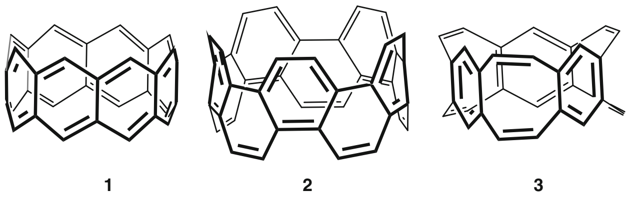

Fig. 1 Three types of nanorings: [8]cyclacene (**1**), cyclo[10]phenacene (**2**), and [6,8]$_3$cyclacene (**3**)

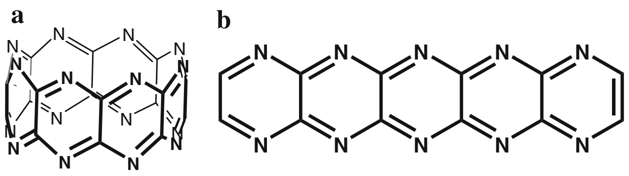

Fig. 2 **a** [8]Pyrazine nanoring, representing one of the eight scrutinized nanorings. **b** [5]Pyrazine nanoribbon, a sample from eight scrutinized nanoribbons

material in field-effect transistors owing to its high charge-carrier mobility [27–29]. Recently, functionalized heptacenes have been synthesized and crystallized [30–32], while larger polyacenes remain elusive. Several theoretical studies have attempted to explain the high reactivities of large polyacenes by designating their electronic properties [11, 33–40]. Houk et al. [13] have predicted a triplet ground state for acenes with $n > 8$. Others have suggested an open-shell singlet ground state for those with $n > 6$ [41–43].

There has been much interest in zigzag-edged graphene nanoribbons (ZGNR) which can be viewed as parallel cross-linked polyacetylene chains [44–50]. Since polyacenes are practically the narrowest ZGNRs, it is suggested that they share a common ground state with wider analogs [24]. In other words, the AFM ground state of ZGNRs agrees with that reported for polyacenes [44, 51]. Moreover, the appearance of the AFM phase can be used as an indicator for cyclacenes' and acenes' chemical reactivity.

Some studies have focused on heterocyclic cyclacene and polyacene derivatives, where the potential of nitrogen-containing oligoacenes as *n*-channel organic semiconductors has been demonstrated [23, 52–55]. Besides, the successive replacement of the CH moieties by nitrogen atoms in these structures offers a number of opportunities to manipulate and control the molecular electronic properties, stabilities, and crystal structures of these materials. "Thus, improved stability toward photooxidation or Diels–Alder dimerization (two major degradation pathways in pentacene semiconductors), can be expected, and depending on the heteroatomic substitution pattern (polarity), improved solubility might be achieved as a basic prerequisite for solution-processing" [53]. Perhaps the most interesting question is: how does substitution of CH by N modify the electronic ground states of azacyclacenes and azapolyacenes?

In response to this question and in order to make the effects of nitrogen atoms more conspicuous, we scrutinized carbon–nitrogen cyclacenes and their analogous polyacenes in the form of pyrazine nanorings and pyrazine nanoribbons at a reasonable theoretical level (Fig. 2). Actually, we have been encouraged by the fact that some acenes which contain pyrazine moieties are already synthesized [56, 57]. So we hope our N-substitutions may bring about changes in the electronic structures of the scrutinized species [58] and lead to a decrease in their reactivity, opening the way for their possible synthesis, and become instrumental in furthering our understanding of CNTs and ZGNRs in the long run.

Results and discussion

In order to alter the electronic ground states of cyclacenes and polyacenes we made an attempt to calculate the effects of nitrogen atom substitutions, forming pyrazine nanorings and pyrazine nanoribbons (Fig. 2). More specifically, the pyrazine nanorings consist of carbons and nitrogens with the general formulae of $(CN)_{2n}$ without any hydrogen.

The two possible electronic ground states investigated are triplet and singlet. The latter is described with the open-shell (OS) UBS (unrestricted broken spin-symmetry) theory, and the restricted closed-shell (CS).

The wave functions appear unstable at the RB3LYP/6-31G* level of theory for all structures except $n = 5$, 10, and 12. Trying to find stable ground states leads to the triplet states for $n = 8$ with rather small triplet–singlet gaps ($\Delta E_{\mathrm{T-CS}} = -8.54$ kJ/mol) (Fig. 3a).

Reoptimizations using the unrestricted broken symmetry B3LYP method (UBS-B3LYP) [19, 41] shows open-shell singlet states ($\mathrm{S_{OS}}$) for $n = 6$, 7, and 11 to be 129.32, 7.06, and 55.69 kJ/mol, respectively, lower than their corresponding closed-shell ($\mathrm{S_{CS}}$) (Fig. 3a). Hence, these species have open-shell singlet ground states displaying rather large spin contaminations ($\langle S^2 \rangle = 1.07$, 2.25) and emerging with radical characters (i.e., antiferromagnetic, AFM) [19]. The AFM ground states are pictured in a way that the α-spin electrons are mainly localized on one edge, while β-spin electrons are on the other edge of the cyclacenes [19, 24], resembling the electronic structures of rectangular polycyclic aromatic hydrocarbons [69] and tetramethylenebenzene [70].

The $\Delta E(\mathrm{S_{OS}} - \mathrm{S_{CS}})$ values for $n = 5$, 10, and 12 approach zero indicating that the open-shell singlets relax to the closed-shell singlet ground states (Fig. 3a) [19]. Increasing the size of the nanorings in the odd and even

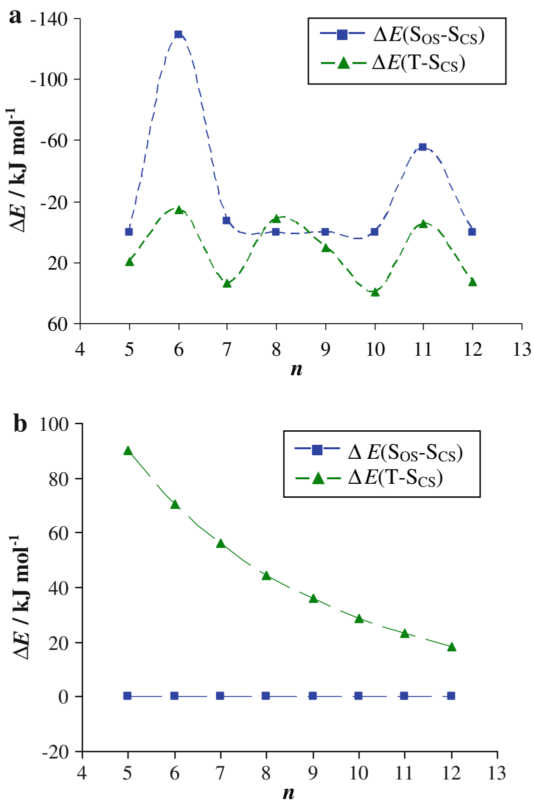

Fig. 3 Energy differences between the (UBS) open-shell singlet (S_{OS}) and closed-shell singlet (S_{CS}) states, $\Delta E(S_{OS} - S_{CS})$, and the energy differences between the triplet (T) and S_{CS} states, $\Delta E(T - S_{CS})$, as a function of n in **a** [n]pyrazine nanorings and **b** [n]pyrazine nanoribbons

series is noteworthy. For instance, in the even series, an open-shell singlet is found for $n = 6$, whereas a triplet is seen for $n = 8$. Further stretch to $n = 10$ and 12 shows closed-shell ground states. In the odd series [5]pyrazine cyclacene is a closed-shell singlet, whereas $n = 7$ and 11 render open-shell singlet ground states appearing similar to that reported for cyclacenes. For $n = 9$ open-shell and closed-shell emerge with the same energy [$\Delta E(S_{OS} - S_{CS}) = 0$]; at this point in conformity with $n = 7$ and $n = 11$ one may assume an open-shell singlet ground state for $n = 9$. On the other hand, squeezing the size of the nanorings to $n = 4$ gives an unusual and unstable structure with an imaginary frequency (NIMAG = 1).

The natural bond orbital (NBO) charge analyses of the pyrazine cyclacenes show significant π electron polarization from carbons toward the more electronegative nitrogen atoms. Specifically, for odd nanorings the absolute values of charges on carbon and nitrogen atoms appear inversely proportional to the size of the ring (Table 1). Such π electron polarization induces the lowering of the energy levels of pyrazine cyclacenes compared to unsubstituted cyclacenes (Fig. 4; Table 2). Larger band gaps ($\Delta E_{\text{LUMO-HOMO}}$) are encountered for the former, compared to the corresponding cyclacenes. Apparently lowering of the energy levels mostly in the even pyrazine nanorings has compensated the pairing energy required for their observed closed-shell electronic configurations (Table 2). Such lowering of the energy level increases with the increase of the size of the nanorings due to the higher frontier orbital perturbations by the greater number of nitrogen atoms. So, for the even pyrazine cyclacene the ground state alters from open-shell in $n = 6$ to closed-shell in $n = 12$. As for cyclacenes and odd pyrazine nanorings ($n = 7$, 9, and 11), the observed open-shell antiferromagnetic ground states stem from the electron–electron repulsions which are not compensated by the energy levels lowering [44]. Therefore, the highest impact of N-substitution on the ground state multiplicity is observed for the even nanorings.

For nanorings with odd n, the $\Delta E_{\text{LUMO-HOMO}}$ drops from about 2 eV (insulator-like character: $n = 5$, 7) to around 1 eV (semiconductor character: $n = 11$) (Table 2).

Table 1 NBO atomic charge of the [n]pyrazine nanorings and [n]pyrazine nanoribbons at the B3LYP/6-31G*//B3LYP/6-31G* level

n	[n]Pyrazine nanorings		[n]Pyrazine nanoribbons	
	C	N	C	N
5	0.39	−0.39	0.332/0.335	−0.362/−0.364
6	0.35	−0.35	0.334/0.336	−0.361/−0.364
7	0.37	−0.37	0.336/0.338	−0.359/−0.360
8	0.35	−0.35	0.339/0.341	−0.359/−0.360
9	0.36	−0.36	0.340/0.343	−0.358/−0.360
10	0.35	−0.35	0.341/0.342	−0.358
11	0.36	−0.36	0.343/0.345	−0.357/−0.359
12	0.35	−0.35	0.343/0.346	−0.357/−0.358

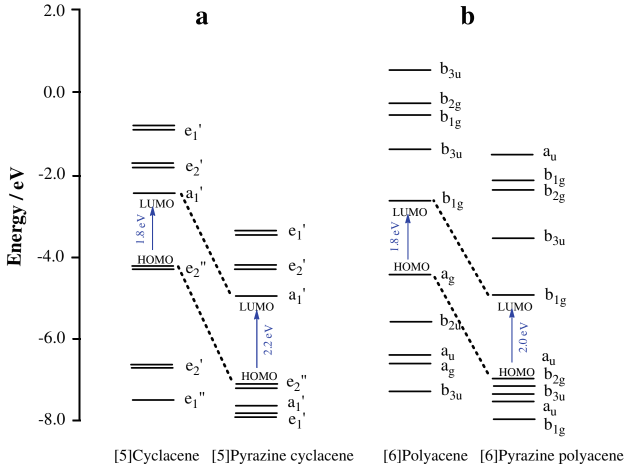

Fig. 4 Lowering of frontier molecular orbital energy levels due to nitrogen atom perturbations: **a** [5]pyrazine cyclacene versus [5]cyclacene, **b** [6]pyrazine polyacene versus [6]polyacene

Table 2 NBO-calculated energies (eV) of the frontier molecular orbitals (E_{HOMO}, E_{LUMO}, $\Delta E_{\mathrm{HOMO-LUMO}}$), for closed-shell [*n*]pyrazine nanorings and [*n*]pyrazine nanoribbons, compared to their corresponding carbon analogues (from Ref. [19] and [41]), at the B3LYP/6-31G*//B3LYP/6-31G* level

n	[*n*]Pyrazine nanorings			[*n*]Pyrazine nanoribbons		
	E_{HOMO}	E_{LUMO}	$\Delta E_{\mathrm{HOMO-LUMO}}$	E_{HOMO}	E_{LUMO}	$\Delta E_{\mathrm{HOMO-LUMO}}$
5	−7.180 (−4.299)[a]	−4.968 (−2.449)	2.212 (1.850)	−6.932 (−4.60)[b]	−4.614 (−2.39)	2.318 (2.21)
6	−7.107 (−3.782)	−5.747 (−2.558)	1.360 (1.224)	−6.989 (−4.41)	−4.941 (−2.61)	2.048 (1.80)
7	−7.341 (−4.054)	−5.292 (−2.394)	2.048 (1.659)	−7.038 (−4.27)	−5.198 (−2.78)	1.841 (1.49)
8	−7.412 (−3.891)	−6.253 (−2.775)	1.158 (1.115)	−7.076 (−4.16)	−5.405 (−2.91)	1.671 (1.25)
9	−7.394 (−3.918)	−5.881 (−2.775)	1.512 (1.143)	−7.109 (−4.08)	−5.576 (−3.01)	1.534 (1.06)
10	−7.522 (−3.918)	−6.526 (−2.911)	0.995 (1.006)	−7.142 (−4.01)	−5.718 (−3.10)	1.424 (0.92)
11	−7.421 (−3.838)	−6.243 (−3.014)	1.177 (0.823)	−7.171 (–)	−5.841 (–)	1.329 (–)
12	−7.565 (−3.938)	−6.694 (−3.027)	0.871 (0.911)	−7.194 (–)	−5.947 (–)	1.247 (–)

[a] Frontier molecular orbital energies (eV), extracted from NBO-calculated data on the optimized structures of Ref. [19]

[b] Molecular orbital energies are taken from Ref. [41]

In contrast, for $n = 6$–12 going from the lower to higher values of even *n* makes the corresponding $\Delta E_{\mathrm{LUMO-HOMO}}$ decrease very slowly (semiconductor character, ca. 1 eV).

The geometrical parameters of closed-shell, open-shell, and triplet states of pyrazine nanorings are instructive. Except for the triplet odd pyrazine nanorings which show C_{2v} symmetry, all singlet ground states and even triplets show D_{nh} symmetry. Specifically, they have two distinct bonds: the peripheral CN bonds whose lengths (1.344–1.356 Å) fall in a range between the reported C=N (1.293 Å) and the C–N (1.470 Å); and the C–C bonds (1.461–1.506 Å) that connect the two trannulenes by sp^2–sp^2 single bonds. For the case of [$4k + 2$]trannulenes in the odd pyrazine nanorings, each trannulene is aromatic and stable. Hence, there is no coupling between the two trannulene chains. Coupling of the two [4*k*]trannulene moieties through C–C bonds gives aromatic stability to the resulting [2*k*]cyclacenes (Fig. 5).

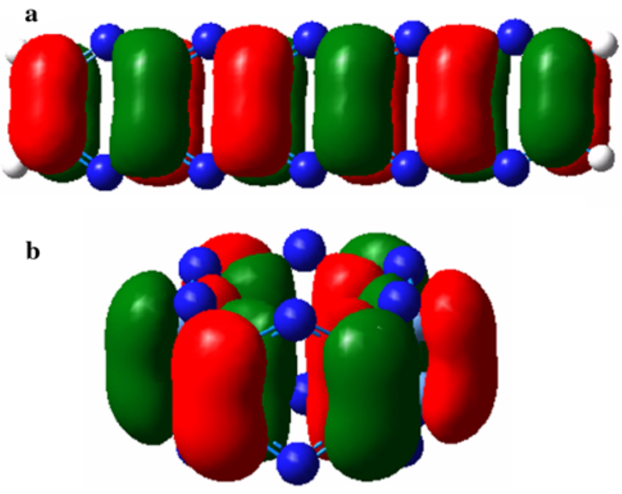

Fig. 5 Frontier molecular orbital for **a** [*n*]pyrazine polyacene, where $n = 5$, showing two –(C=N)$_5$– interchain intractions, **b** [6]pyrazine nanoring showing two trannulene interchain intractions

The nucleus-independent chemical shift (NICS) values are often calculated in order to obtain a feel for aromaticity in the nanoring cavity centers (G) [2, 21] and on the surface of the benzenoid rings. Our nanoring centers of the cavity (G) show significantly negative NICS values, with the exception of the largest odd nanorings $n = 11$ (Fig. 6). The NICS values of the benzenoid rings appear also substantially negative for the even pyrazine nanorings, while no aromaticity is encountered for the odd ones. The maximum NICS value is obtained for −1.0 Å. This is consistent with the inner π-electron density, which appears more conglomerated. Moreover, NICS decreases in going from −1.0 Å below the benzenoid ring centers (inside the nanoring) to 1.0 Å (outside the nanoring). In fact, such difference in NICS values on the convex and concave sides of the nanorings should not be associated with aromaticity, as this difference rather is a manifestation of different electron densities in the vicinity of the surfaces.

Nanorings exert a strain on their constituting benzenoid rings which is decreased through the increase of their size. Hence plotting the [*n*]pyrazine nanorings energy/*n* against the number of benzenoid rings (*n*) indicates the gain of relative stability attributed to the release of strain from the constituting benzenoid rings per se, in going from $n = 5$–12 (Fig. 7a).

In contrast to a previous report which suggests open-shell singlet diradical ground states for the large polyacenes [41–43], nitrogen substitution gives closed-shell (nonmagnetic) ground states for [*n*]pyrazine nanoribbons with $n = 5$–12, showing zero spin contaminations ($\langle S^2 \rangle = 0$). This conclusion is manifested through the results obtained from plotting the changes in energies of

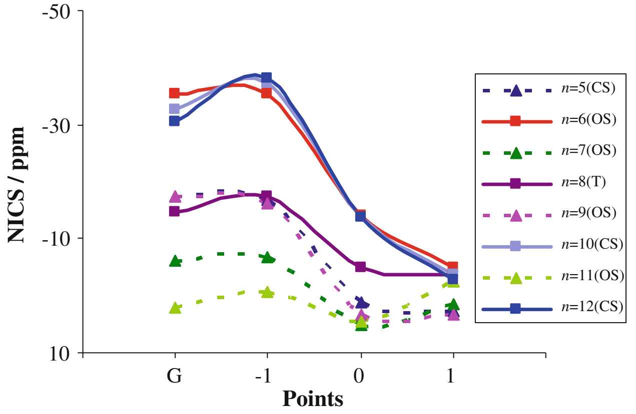

Fig. 6 Changes of the total NICS/ppm 1 Å above the benzenoid ring centers to 1 Å below, including the cavity centers of [*n*]pyrazine nanorings (*G*), for $n = 5$–12, where *CS* closed-shell, *OS* open-shell, *T* triplet

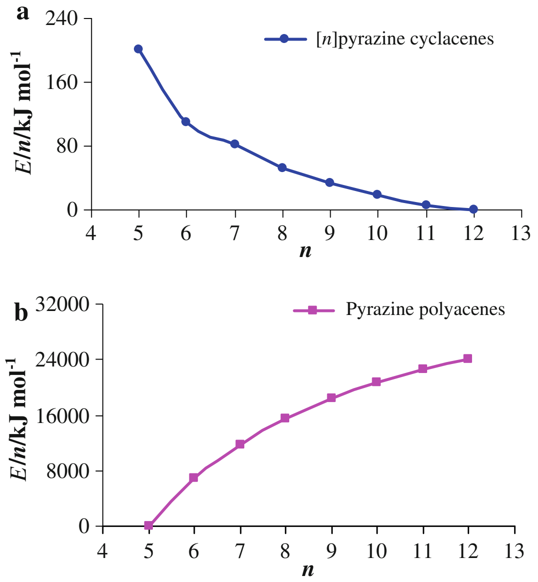

Fig. 7 Relative energies per subunit (*E*/*n*) for **a** [*n*]pyrazine cyclacenes, and **b** [*n*]pyrazine polyacenes where $n = 5$–12. The lowest energy is set at 0.0 kJ/mol

the triplet and S_{OS} (relative to that of S_{CS}) for [*n*]pyrazine nanoribbons against the number of the fused benzenoid rings (*n*) (Fig. 3b).

Similar to the case of nanorings which was discussed above, the NBO charge analysis for the pyrazine nanoribbons is instructive (Tables 1, 2). It shows π electron transfer from carbon to the more electronegative nitrogen atoms, inducing a partially negative charge on nitrogen. Again, such π electron polarization is translated into the lowering of the energy levels of N-substituted polyacenes compared to unsubstituted ones (Fig. 4; Table 2). Larger band gaps ($\Delta E_{\mathrm{LUMO-HOMO}}$) are encountered for the [*n*]pyrazine nanoribbons compared to the corresponding polyacenes giving closed-shell (nonmagnetic) singlet ground states for $n = 5$–12. Moreover, the $\Delta E_{\mathrm{LUMO-HOMO}}$ decreases moderately from $n = 5$ (insulator-like character) to $n = 12$ (semiconductor character) (Table 2).

Closed-shell and open-shell structures have very similar geometries. Neglecting the terminal benzenoid rings, they resemble two non-alternating –(C=N)$_n$– ribbons arising from a lack of Peierls' distortion in each ribbon, which are joined by sp^2–sp^2 single bonds and show very weak π interactions. This pattern has been rationalized previously for polyacenes [11, 41]. The interchain couplings between the MOs of two –(C=N)$_n$–ribbons appear in the MO shapes (Fig. 5).

Similar to polyacene all the pyrazine analogues are aromatic (negative NICS values) with their inner rings being more aromatic than the corresponding outer ones (Fig. 8) [71]. The changes of the energy of [*n*]pyrazine nanoribbons/*n* reveals instability in going from $n = 5$–12 (Fig. 7b).

Conclusion

A computational account of the electronic and aromatic characters of N-substituted cyclacenes and polyacenes is presented. The even [6]pyrazine nanorings appear as an open-shell singlet (antiferromagnetic), while the [8]pyrazine nanoring has a triplet ground state (ferromagnetic). Further stretch to [10]- and [12]pyrazine nanorings bring about closed-shell singlets (nonmagnetic). On the other hand, nanorings with odd *n* (except $n = 5$) appear with open-shell singlet ground states. Rather large [*n*]pyrazine nanoribbons are found to possess nonmagnetic closed-shell singlet ground states. The energy gaps for all the scrutinized odd and even pyrazine nanorings appear inversely proportional to their corresponding diameter. Similar to polyacenes, all the pyrazine analogues are aromatic with their inner rings being more aromatic than their corresponding outer rings. Moreover, the $\Delta E_{\mathrm{LUMO-HOMO}}$ moderately decreases from $n = 5$–12.

Finally, the pyrazine cyclacene and pyrazine polyacene systems invite experimental explorations, with the potential applications including utilization as organic semiconductors, organo-magnetic materials, and molecular electronic devices. Moreover, replacement of CH moieties of cyclacenes with nitrogen atoms induces partial positive charges on the carbons and negative charges on the edge nitrogens. Such point charges raise the storage capacities of pyrazine cyclacenes and increase the possibility of their usage as host materials [72, 73].

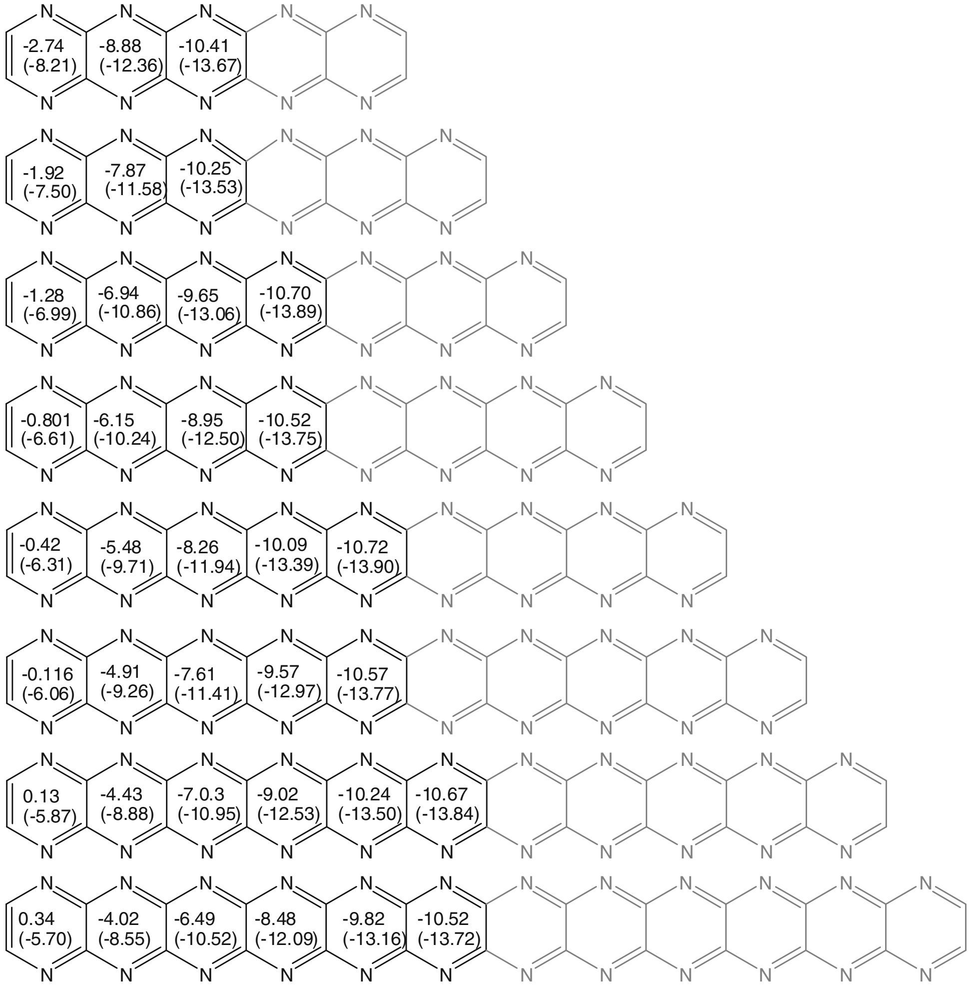

Fig. 8 NICS (0) and NICS (1) (in *parenthesis*) for the center of the benzenoid rings of [*n*]pyrazine nanoribbons, where $n = 5$–12

Computational details

The geometries of all structures were optimized without any symmetry constraints at the B3LYP/6-31G* DFT level [59–63], using the Gaussian 98 program [64]. The NBO population analyses [65, 66] were accomplished at the same level of theory. To derive the NICS data, single-point GIAO-NMR [67, 68] calculations with B3LYP/6-31G* were carried out. Harmonic vibration frequency analyses were also performed—at the same level of theory used for optimization—to check whether the obtained structure is a minimum on its potential energy surface.

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