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Aromaticity of the planar hetero[8]circulenes and of their doubly charged ions: NICS and GIMIC characterization

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A series of planar hetero[8]circulenes and of their doubly charged ions is studied by the NICS and GIMIC methods to interpret the aromatic properties of these high symmetry species. In accordance with the performed calculations all studied hetero[8]circulenes are found to be nonaromatic compounds because of paratropic and diatropic ring-currents are completely canceled yielding almost zero net current. In a great contrast, the dicationic and dianionic hetero[8]circulenes demonstrate the predominant contribution of diatropic ring currents resulting in the total aromatic character of the studied doubly charged ions. This fact allows us to predict the high stability of dianionic hetero[8]circulenes and to explain extremely high stability of dicationic species observed in the mass-spectra.

Introduction

Hetero[8]circulenes ‡ represent a quite extensive class of heterocyclic polyaromatic compounds consisting of two concentric annulene rings similar to other heterocirculenes.[1] All hetero[8]circulenes consist of inner eight-membered cyclooctatetraene (COT) ring with 8π electrons and the outer 24π-electronic ring. Some of the hetero[8]circulenes are presented in Fig. 1. Compounds **1–5** are really synthesized[2] (azaoxa[8]circulenes[2d, 2e] **4** and **5** are presented here without alkyl-substituents, for simplicity) whereas compounds **6** and **7** are hypothetically designed (not isolated in the individual state[3]) and are interesting for us in order to investigate their aromaticity with the increasing number of Nitrogen atoms in the outer perimeter.

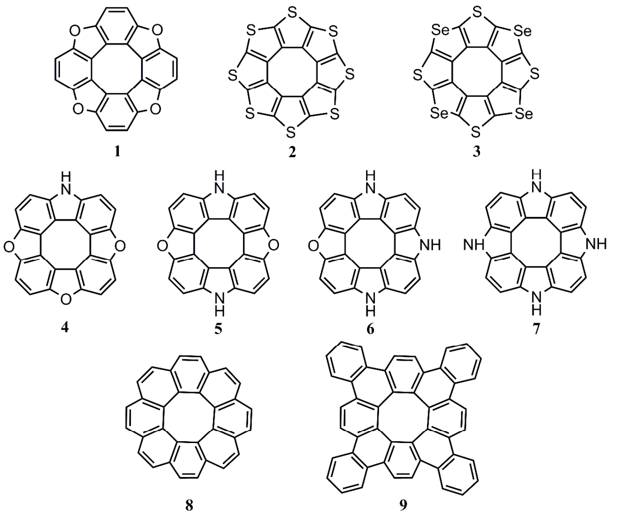


Fig. 1. Molecular structures of the series hetero[8]circulenes **1–7**.

As one can see from the Fig. 1, the outer ring of the hetero[8]circulenes consists of various type of heteroatoms (O, S, N, Se) in a contrast to the recently synthesized [8]circulene[4] **8** and tetrabenzo[8]circulene[5] **9,** both being of the totally hydrocarbon-type compounds. All hetero[8]circulenes **1–7** are the valence-isoelectronic analogouses of [8]circulene. However, the great difference between these two types should be mentioned: all hetero[8]circulenes **1–7** are absolutely planar in a contrast to the saddle-shaped circulenes **8** and **9**.[4–6] The planar structure of hetero[8]circulenes determines their specific aromatic properties. It was recently shown independently by us[7] and by Radenković et. al.[8] that the central ring of the tetraoxa[8]circulenes is antiaromatic, whereas each of the condensed benzene and furan rings are aromatic. The similar results were obtained for the "sulflowers" **2** and **3** by Gahungu and Zhang[9] and for the azaoxa[8]circulenes **4** and **5** by Pittelkow et. al.[2d, 2e] being based on nucleus-independent chemical shifts (NICS) indexes calculations. Thus, the common feature of the compounds **1–5** consists of the fact that the inner COT ring is antiaromatic[10] and the surrounding systems of five- and six-membered rings are fully aromatic. In this way, the "annulene within an annulene" model[8,11] of aromaticity is not applicable for the circulenes **1–5** and their analogs. At the same time, the aromaticity concept in its classical definition is usually and conventionally accepted for the molecule as a whole,[12] whereas the NICS indexes do characterize the definite ring. If we consider the monocyclic system (benzene or cyclobutadiene, for example), the NICS parameter fits well to the classical aromaticity interpretation based on the dominating role of the "aromatic" diatropic ring currents for benzene molecule and "antiaromatic" paratropic ring currents for the cyclobutadiene compound.[13] Thus, the positive NICS indexes, calculated in the center of the cyclobutadiene ring assume the antiaromatic character of the whole cyclobutadiene molecule, while the corresponding significantly negative NICS indexes for the benzene ring denote the aromatic character of this chemical compound.[13]

We want to stress, that the aromaticity definition for the hetero[8]circulenes **1–7** represents a more complicated task in comparison with the simple benzene and cyclobutadiene examples. The NICS criterion correctly describes the local aromatic character of each benzene, furan, pyrrol, thiophene and selenophene rings and the local antiaromatic character of the inner COT. But the question arises: what is the true (totally aromatic, antiaromatic or nonaromatic) character of the whole hetero[8]circulene molecules? The answer to this question can be provided by the gauge-including magnetically induced currents (GIMIC) calculations.[14] It is described in Ref.[14a] that the GIMIC method (like the NICS concept) is based on the gauge-including atomic orbitals (GIAOs) approximation and provides the detailed information about electron delocalization properties, aromatic character, and magnetically-induced current pathways in molecules. The GIMIC method is proven very useful for aromaticity investigation of the specific molecules such as fullerene C_{60} and their multicharged C_{60}^{10+} ion, [n]cycloparaphenylenes, nano-sized hydrocarbons etc.[14a]

In the present work the GIMIC calculations of the ring-current densities have been applied to the hetero[8]circulenes **1–7** for the first time together with additional comparison of the calculated NICS indexes. The second task, considered in the present paper, concerns aromaticity of the doubly charged ions of the studied hetero[8]circulenes **1–7**. The dications of the tetraoxa[8]circulene **1** and "sulflower" **3** were clearly identified in the mass-spectra of these compounds.[2c,15] Moreover, the dication $\mathbf{1}^{2+}$ is stable enough to produce the $\mathbf{1}^{3+}$ species in the mass-spectrum. Such unusual stability of the multicharged tetraoxa[8]circulene **1** cations just motivate us to predict and design the structure, vibrational spectra and aromatic properties of the doubly charged ions of hetero[8]circulenes **1–7** (including their dianions). The single ionized species **1–7** are also described in the present work These results are complementary to our previous NICS calculations for the doubly ionized tetraoxa[8]circulene **1** and azaoxa[8]circulenes **4** and **5**.[2d,2e] In particular, it was found that the inner COT rings retain their antiaromaticity upon double oxidation (2+), whereas in the doubly reduced (2-) species the COT ring occurs to be aromatic (large negative NICS(0) and $\mathrm{NICS(1)}_{zz}$ values). In all doubly ionized species studied, the benzene, furan, and pyrrole rings appear to retain their aromaticity.[2d,2e]

Computational methods

The equilibrium geometrical parameters of the **1–7** molecules and their ionized forms were calculated by the DFT/B3LYP[16] method with the control of possible symmetry constrains using the 6-31+G(d)[16c] basis set with the GAUSSIAN 09 package[17] (the open-shell doublet and triplet states were calculated by the spin-unrestricted UB3LYP method with the same basis set). All vibrational frequencies for the studied molecules and ions were found to be real which indicates that a true minimum on hypersurface of the total energy was found for all systems. The I1 values are varying in the range of 5.95-7.13 eV and are comparable with the energies of chemical bonds; the second ionization potential for the studied compounds **1–7** is about 10 eV indicating the relative ease of dicationic species formation.[2j] The studied molecules are characterized by the small negative first electron affinity values (Table 5) which correspond to the exothermic process of the anions formation. The second electron affinity values are moderately positive, which corresponds to the endothermic effect, indicating the true possibility of the **1-7** dianions formation. In this way, we have demonstrated the additional evidence of the principal possibility for existence of the stable doubly charged ions of compounds **1-7**. The NICS indexes[12,13] for the studied species were calculated at the center of each ring (denoted as NICS(0)) and at the 1 Å distance above the plane of the ring (NICS(1)) at the B3LYP/6-311++G(d,p)[16d] level of theory with the GIAO[18] approximation. The NICS(1) indexes are recommended to account for the π-electron delocalization,[12b,13a] while NICS(0) are considered for estimation of the total σ+π-electron delocalization effects.

The magnetically induced current densities were calculated with the GIMIC method.[14] The nuclear magnetic resonance (NMR) shieldings were obtained using Turbomole software package[19a] for calculation of the ring-current susceptibility (in nA T^{-1}) which is denoted as the ring-current strength[14a] in the next chapters of the article. The current strengths can be used as an aromaticity index (the current strength for the aromatic benzene molecule is significantly positive and equal to 11.8 nA/T at the B3LYP/TZVP level comparing with -19.9 nA/T for antiaromatic cyclobutadiene and 0.2 nA/T for the nonaromatic cyclohexane compound).[14a] Current density plots have been generated with the JMOL package.[19b]

All calculations were performed on the PDC supercomputers of the Royal Institute of Technology (Stockholm), CSC – the Finnish IT Center for Science (Finland) and at the Tomsk State University (SKIF, Russia).

Results and discussion

Structural parameters. The optimized geometrical parameters (including bond lengths and the optimized Cartesian coordinates) of all hetero[8]circulenes **1–7** and their ionized forms are presented in ESI† (Figs. S1, S3). An important observation is that all neutral molecules **1–7** and corresponding oxidized compounds (1+ and 2+ ions) exhibit planar structure. Anionic (1-) and dianionic (2-) species of the tetraoxa[8]circulene **1** are also planar in a great contrast to the anionic circulene **2–7** species, which have deviated from the planar structure in the both anionic (1-) and (2-) states. As one can see from the Fig. 2 the planar skeleton of azaoxa[8]circulene **7** is slightly distorted upon successive reduction because of the Nitrogen atoms occur to be sp^3-hybridized. The analogous structural deformation is also observed for other azaoxa[8]circulenes **4–6** upon electron attachment. At the same conditions, "sulflowers" **2** and **3** are distorted increasingly and are transformed into the bowl-shaped dianionic species (Fig. 2, right side) in a good agreement with results of Ref.[20] Additionally, we need to note that the $\mathbf{3}^{2-}$ ion is strained enough to break one of the Se–C bonds and to be transformed into the twisted compound (Fig. S2, ESI†).

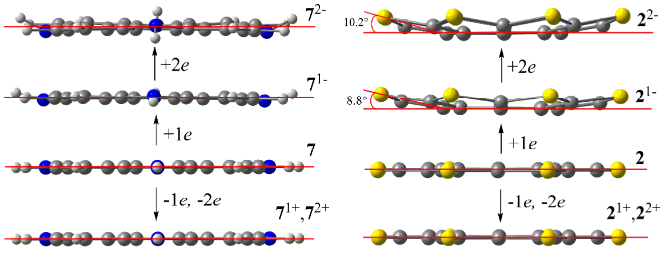


Fig. 2. The change of molecular structure for the compounds **2** (right side) an **7** (left side) upon the reduction and oxidation processes.

A distinctive feature of all circulenes presented in Fig. 1 is the high molecular symmetry which determines the specific bond alternation in the inner COT. In this way it is interesting to compare the structural features of the central eight-member ring with the similar systems and other circulenes (Tables 1, 2). In particular, the **1, 3** and **7** molecules belong to the D_{4h} symmetry point group in the ground singlet state ($^1A_{1g}$). The inner octatetraene cycle of these compounds has a strict system of the short (1.396, 1.439 and 1.412 Å for molecules **1, 3** and **7,** respectively) and long (1.431, 1.441 and 1.439 Å, respectively) C–C bonds in a good agreement with the X-ray data[21] and previous quantum-chemical calculations[3,10,20,22] (Tables 1, 2). The short bonds belong to benzene/thiophene rings, and the long bonds are fused with the furan/pyrrol/selenophene cycles. The "sulflower" **2** species is a standalone representative of the hetero[8]circulenes because of the highest D_{8h} symmetry.[2b,21e,23] All C–C bonds of the inner COT are absolutely equivalent and are equal to 1.425 Å (exp.: 1.419 Å). Upon the one- or two-electron attachment to compound **2** all C–C bonds in the COT core remain equivalent (1.436 and 1.444 Å for the $\mathbf{2}^{1-}$ and $\mathbf{2}^{2-}$ ions respectively). But upon oxidation impact the inner COT becomes alternated and the short (1.409 and 1.390 Å for the $\mathbf{2}^{1+}$ and $\mathbf{2}^{2+}$ ions) and long (1.423 and 1.410 Å, respectively) C–C bonds appear.

Table 1. Calculated bond lengths (Å) in the inner COT for the "sulflower" **2** and **3** molecules and for their doubly charged ions.

	M	$(C–C)_S$	$(C–C)_{Se}$
2	1	1.425 / 1.420,[a] 1.418[b] / (1.419)	–
$\mathbf{2}^{2+}$	3	1.410, 1.399	–
$\mathbf{2}^{2-}$	1	1.444	–
3	1	1.439 / 1.429[a] / (1.433)	1.441 / 1.431[a] / (1.436)
$\mathbf{3}^{2+}$	3	1.416, 1.428	1.416÷1.423
$\mathbf{3}^{2-}$	1	1.445÷1.461	1.445÷1.494

M – ground state spin multiplicity; X-ray experimental data[2b,21d] are presented in parentheses; [a] – Ref.[20], [b] – Ref.[24]; $(C–C)_S$ and $(C–C)_{Se}$ denote the C–C bonds in the thiophene and selenophene rings, respectively.

Table 2. Calculated bond lengths (Å) in the inner COT for the tetraoxa[8]circulene **1**, aza[8]circulenes **4, 7** molecules and for their doubly charged ions.

	M	$(C–C)_b$	$(C–C)_O$	$(C–C)_N$
1	1	1,396 (1.406)	1.431 (1.421)	–
$\mathbf{1}^{2+}$	1	1.438	1.386	–
$\mathbf{1}^{2-}$	1	1.423	1.405	–
4	1	1.403, 1.396 (1.405, 1.399)	1.430, 1.434 (1.434, 1.441)	1.434 (1.423)
$\mathbf{4}^{2+}$	1	1.447,1.436	1.398, 1.386	1.385
$\mathbf{4}^{2-}$	1	1.428, 1.423	1,409, 1.405	1.414
7	1	1.412 / 1.401[a]	–	1.439 / 1.440[a]
$\mathbf{7}^{2+}$	1	1.371	–	1.475
$\mathbf{7}^{2-}$	1	1.434	–	1.420

M – ground state spin multiplicity; X-ray experiment data[2d] are presented in parentheses; [a] – Ref.[3a]; $(C–C)_b$, $(C–C)_O$ and $(C–C)_N$ denote the C–C bonds owned to benzene, furan and pyrrole rings, respectively.

Azaoxa[8]circulenes **4–6** belong to the C_{2v} (**4** and **6**) and D_{2h} (**5**) symmetry point groups. These compounds have the similar structural parameters for themselves and compound **7**: the bond lengths in the inner COT are varied in the short ranges 1.403–1.404, 1.430–1.438 and 1.434–1.443 Å for the benzene, furan and pyrrol rings, respectively. The structural parameters for ionized species of compounds **4–7** are also similarly close.

Summing up the structural part of the paper we can conclude, that the molecular geometry of all circulenes **1**–**7** is usually distorted to the lower symmetry point groups upon the oxidation or reduction impact comparing with the neutral species. At the same time the alternation of the short and long C–C bonds is also changed for the inner COT (Tables 1, 2). In connection with this fact, the structural features of the neutral and ionized hetero[8]circulenes **1–7** should provide strongly different aromatic properties. We also found, that the difference of the short and long C–C bonds in the inner COT of circulenes **1**–**7** is varied in a small range and does not exceed 0.034 Å which is much shorter in comparison with the bond difference (0.121 Å) for the strongly antiaromatic free COT of the D_{4h} symmetry, hypothetically predicted and studied in Ref.[25]. In this way, we have predicted the much weaker antiaromatic character for the annelated COT of the hetero[8]circulenes **1-7** in comparison with the planar free cyclooctatetraene.

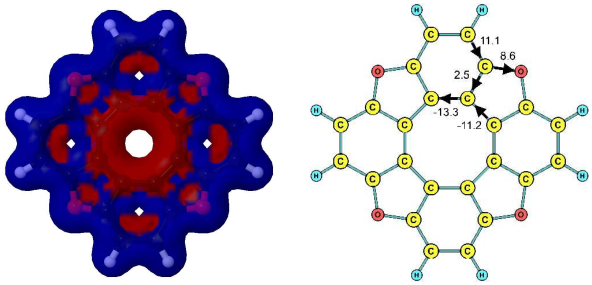
Aromaticity of the neutral hetero[8]circulenes

Table 3 shows the total current strength for hetero[8]circulenes **1**–**7**. It is well known, that for the aromatic species, such as benzene, the diatropic current component on the outside of the molecules dominates over the paratropic current one inside the ring yielding a total diatropic current.[14a] For antiaromatic molecules, such as cyclobutadiene, the paratropic current inside the ring dominates. Nonaromatic molecules also sustain the diatropic and paratropic ring currents, but the two components cancel one another, yielding an approximately zero total current.[14c]

In accordance with the presented classification, all hetero[8]circulenes **1–7** represent nonaromatic species because the paratropic internal currents substantially cancel out the diatropic contribution on the outside edge (Fig. 3, Table 3) analogously to the well known nonaromatic cyclic hydrocarbons and fullerene C_{60}.[14a] These compounds, like our circulenes **1–7**, have strong diatropic currents outside the molecule completely cancelled by the paratropic currents inside it.[14]

Table 3. The total ring current strength (I_{tot}, in $nA{\cdot}T^{-1}$) for the neutral molecules of hetero[8]circulenes **1**–**7** and corresponding NICS indexes (ppm) for the inner COT of the studied compounds

Molecule	I_{tot}	NICS	NICS(1)
1	–2.1	8.35	5.24
2	–0.2	4.60	2.07
3	0.6	5.76	2.97
4	-3.1	8.32	5.13
5	-2.6	8.26	5.08
6	-0.6	8.11	4.95
7	-0.5	7.72	4.74



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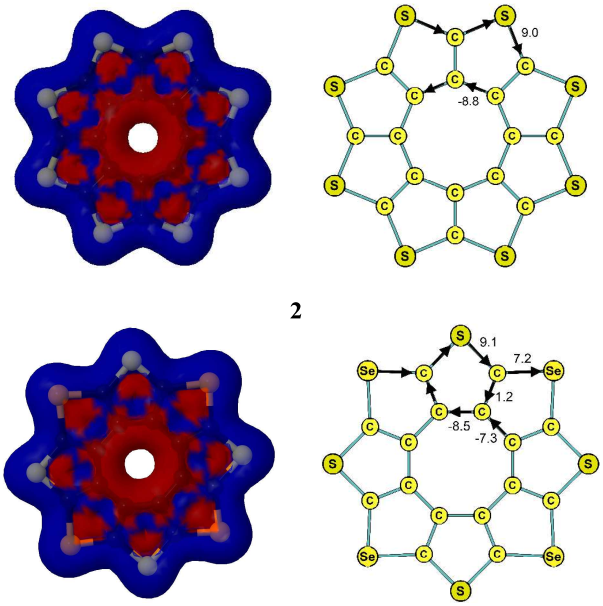

2

3

Fig. 3. The ring-current densities (left) and ring-current strengths (right, nA·T^{-1}) for each bond in the hetero[8]circulenes **1–3** molecules (red and blue colours denote the paratropic and diatropic ring currents, respectively). For the compounds **4–7** see ESI† (Fig. S4).

Our NICS calculations qualitatively confirm the nonaromaticity of hetero[8]circulenes **1–7.** In particular, for all studied neutral hetero[8]circulenes the inner COT core is antiaromatic and characterized by the negative NICS(0) and NICS(1) values which are approximately equal (with the opposite sign) to the corresponding averaged NICS indexes for the five- and six-membered aromatic rings (Figs. S5, S6). Thus, it is correct to consider that the paratropic and diatropic components of the total ring-current **1**–**7** are basically compensated for the **1**–**7** molecules.

An interesting feature of the azacirculenes **4–7** is the rise of the total ring-current strength with an increase of the Nitrogen atoms number (Table 3). As one can see from the Table 3 and Fig. S5 the NICS(0) and NICS(1) indexes for the inner COT core of azacirculenes are monotonously decreased, i.e. paratropic contributions to the net ring current is also reduced inside the **4–7** row. From the other hand, the diatropic component of the net current slightly increases for compounds **4–7** (NICS indexes for pyrrole rings become more negative). Thus, the total ring current of the azacirculenes **4–7** reduces from -3.1 nA·T^{-1} for compound **4** to -0.5 nA·T^{-1} for compound 7, i.e. circulene **4** can be considered as slightly antiaromatic species, whereas circulene **7** is almost nonromantic compound.

Stability and aromaticity of dicationic thio[8]circulenes

The "sulflowers" **2** and **3** correspond to the D_{8h} and D_{4h} symmetry point groups, respectively. Due to the high symmetry the bonds alternation in the inner COT core is absent for compound **2** and almost absent for the compound **3** (Table 1). One should note that the **2** and **3** molecules are characterized by the strict double degeneracy of the highest occupied molecular orbitals (HOMO). In this way it is logical to predict, that the double oxidation of the "sulflowers" molecules could lead to formation of the triplet state dications in accordance with molecular analogous of the Hund's rule (Fig. 4). This proposal was predicted in Ref.[26] without any theoretical and experimental evidences. Our DFT-calculations confirm that the dications of compounds **2** and **3** have the ground electronic triplet state. Moreover, thiophene and selenophene rings are predicted to be aromatic it the triplet state because the corresponding NICS(0) and NICS(1) indexes are strongly negative (Fig. 5). The inner COT ring is slightly aromatic for dication **2**$^{2+}$ and almost nonaromatic for the **3**$^{2+}$ ion.

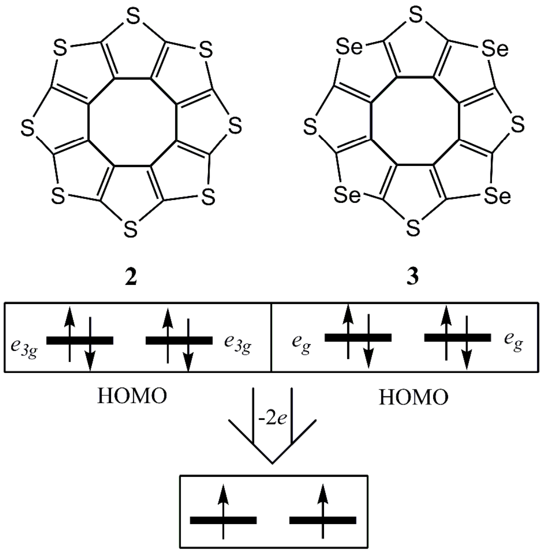

Fig. 4. Formation of the triplet state dications of compounds **2** and **3** upon double oxidation process.

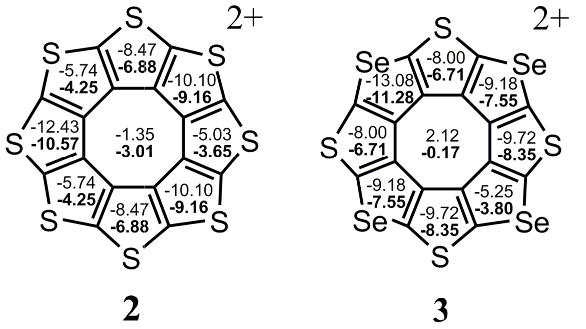

Fig. 5. NICS(0) (top number) and NICS(1) (bottom number in bold) indexes, calculated for the triplet state dications of compounds **2** and **3**.

The singlet electronic states of dications **2**$^{2+}$ and **3**$^{2+}$ are slightly higher in energy (by about 5 kcal mol^{-1} at the DFT/B3LYP/ 6-31+G(d) level) than the corresponding triplet ground states. In addition, all thiophene, selenophene and COT rings in the singlet state of the **2**$^{2+}$ and **3**$^{2+}$ ions are strongly antiaromatic (corresponding NICS(0) and NICS(1) values are significantly positive, Fig. S7). However, the *ab initio* calculations at the CCSD and CASSCF(8,8) levels predict that the **2**$^{2+}$ and **3**$^{2+}$ dications are characterized by the closed-shell singlet ground state (the triplet excited state is higher in energy by about 75 kcal mol^{-1} than the ground singlet state, Table 4) in a great contradiction with the DFT calculations.

Table 4. Relative energy (kcal mol^{-1}) of the exited triplet state of the dicationic compounds **2** and **3** (the total energy of the ground singlet state (S_0) is taken as zero).

Compounds	CCSD/6-31+G(d)	CASSCF(8,8)/6-31+G(d)
2^{2+}	+77.9	+76.2
3^{2+}	+74.1	+67.1

In this way we have concluded that the DFT calculation strongly underestimates the energy of the **2**$^{2+}$ and **3**$^{2+}$ lowest triplet states and probably overestimate their closed shell energy-origin.

Aromaticity of the doubly ionized hetero[8]circulenes

Nowadays the NICS indexes are widely used as a magnetic aromaticity criterion of the multicharged species.[27] Generally, the aromatic properties of the "simple" cations, anions and multicharged ions are strongly differ from the corresponding neutral species.[27] Such the unusual behaviour we have also found for ionized compounds **1–7** (some additional remarks are presented in the previous section devoted to aromaticity of the triplet state sulflowers).

First of all, it is interesting to discuss aromaticity of the doubly reduced (2-) ions of the **1–7** compounds. As a general trend, the dianionic circulenes **1**, **4–7** are predicted to be completely aromatic because of the inner COT core and all surrounding benzene, furan and pyrrole moieties are strongly aromatic (corresponding NICS indexes are significantly negative). In a great contrast, the anionic and dianionic ions of the "sulflover" **2** are predicted to possess a non-aromatic COT core because of significant out-of-plane macrocycle deformation observed (Fig. S2; corresponding NICS indexes approximately equal to zero, Fig. S5). For the **3**$^{1-}$ and **3**$^{2-}$ ions the C–Se bond cleavage is predicted (Fig. S2, ESI†), but other selenophene and thiophene rings retain aromatic character; the inner COT core becomes nonaromatic due to its nonplanar twisted structure. As a result, a predominant diatropic contribution from the selenophene and thiophene rings causes the net aromatic character of the **3**$^{1-}$ and **3**$^{2-}$ ions. It is important to note, that for the (1-) anionic **1**, **4–7** species the inner COT core and surrounding cycles are also aromatic similar to the dianionic analogues (Fig. S3, ESI†).

Figs. S5, S6 additionally contain the values of NICS indixes estimated for cations and dications of compounds **1–7**. The loss of aromaticity is predicted for the five- and six-membered rings (Figs. S5, S6) due to removal of one π-electron from compounds **2–6**, when comparing neutral and cationic structures. As an exception, one-electron removal from the **1** and **7** compounds containing four furan and pyrrole rings, respectively, does not lead to significant changes of their aromatic character (i.e. hetarene and benzene rings stand aromatic, Fig. S5). It is interesting to note, that the double oxidation of the **1, 4–7** circulenes provides a strong increase of the diatropic ring currents in the condensed benzene, pyrrole and furane rings (NICS indexes are twice as much comparing the neutral species). At the same time, the inner COT ring retain antiaromatic for compounds **4–7** (NICS indexes do not much differ comparing with the neutral species); for the **1**$^{2+}$ ion the inner COT core becomes nonaromatic rather than antiaromatic (NICS(0) = 2.5 ppm, but NICS(1) is close to zero, Fig. S5). Thus, we have predicted, that the dicationic **1, 4–7** circulenes do represent the predominantly aromatic species because of diatropic ring currents in the outer macrocycle are much stronger than the paratropic currents induced by the inner COT core. This fact allows us to prove, that the aromaticity of dicationic circulene **1** determines its high stability and very weak fragmentation in the gas phase upon the electron beem impact.[15] The similar stability of dicationic compounds **4–7** should be also predicted.

We have also calculated the first and second ionization energies (*I*) and the electron affinity (*A*) since they directly characterize the stability of the ionized molecules **1–7** (Table 5).

Table 5. The first and second ionization energies (*I*) and the electron affinity (*A*) calculated by the B3LYP/6-31+G(d) method

Compound	I_1, eV	I_2, eV	A_1, eV	A_2, eV
1	7.05	10.85	-0.81	2.78
2	7.13	10.57	-0.46	2.43
3	6.91	10.24	-0.59	1.76
4	6.82	10.58	-0.60	2.95
5	6.54	10.38	-0.40	3.11
6	6.22	10.21	-0.20	3.26
7	5.95	9.84	-0.01	3.41

The I1 values are varying in the range of 5.95–7.13 eV and are comparable with the energies of chemical bonds; the second ionization potential for the studied compounds **1–7** is about 10 eV indicating the relative ease of dicationic species formation.[2j] The studied molecules are characterized by the small negative first electron affinity values (Table 5) which correspond to the exothermic process of the anions formation. The second electron affinity values are moderately positive, which corresponds to the endothermic effect, indicating the true possibility of the **1–7** dianions formation. In this way, we have demonstrated the additional evidence of the principal possibility for existence of the stable doubly charged ions of compounds **1–7**.

Conclusions

Based on the nucleus-independent chemical shifts (NICS) and gauge-including magnetically induced currents (GIMIC) calculations we have shown that the neutral molecules of all planar isoelectronic hetero[8]circulenes **1-7** are almost nonaromatic being formed by a condensed aromatic system (similar to the ribbon of benzene, furane, thiophene, selenophene or pyrrole rings) which surrounds the inner antiaromatic eight-membered cycle.

The selenium containing "sulflower" **2** with 36 π-electrons is characterized by the almost zero diatropic total ring current (0.2 nA T^{-1}) and therefore can be considered as strictly nonaromatic. Other circulenes **1**, **3–7** are also predicted to be nonaromatic with a net paratropic ring-current strength of -3.2 – -0.2 nA T^{-1}. However, the addition of two electrons changes considerably the current strengths for all studied circulenes, presented in Fig. 1. The dianionic hetero[8]circulenes incarnate the complete aromatic systems according to the ring-current criterion. They sustain diatropic ring-currents confirmed by significantly negative nucleus-independent chemical shifts indexes for the inner cyclooctatetraene core (except the bent **1**$^{2-}$ and **2**$^{2-}$ species) and for the benzene and hetarene cycles. Dicationic hetero[8]circulenes also sustain net diatropic ring-currents due to the high diatropic contribution from the benzene and hetarene conjugated rings. Thus, in a general case the two electron attachment or reduction satisfy the (4n+2) Hückel rule for the hetero[8]circulenes molecules. In this way, the dicationic and dianionic hetero[8]circulenes can be assigned as the predominantly aromatic species. This fact provides an unusual stability of the dicationic **1–3** circulenes which are effectively formed in the mass-spectra. High stability of other doubly charged hetero[8]circulenes have also been predicted in the present work. We do not exclude the possibility that the doubly charged hetero[8]circulene ions can be stabilized by complexation with the transition metal clusters.[28]

We want to note in the conclusion part that the synthesis of the doubly charged hetero[8]circulenes is a very difficult task from the chemical point of view. Only limited information is known about generation of hetero[8]circulenes cation-radicals by the chemical oxidation.[2b,29] The anionic and dianionic hetero[8]circulenes are still unknown so far, but the general principal routs to obtain such species are well documented in the literature (slow electron impact, reduction by the alkali metals and other experimental methods).[30]

The ring currents in the studied ionized and neutral systems are directly immeasurable (they can be induced only by an external magnetic field), but they provide contributions to the ^{1}H and ^{13}C chemical shifts which are usually NMR-measured with the high accuracy. For intrans, in Ref.[31] the tetra-*tert*-butyl substituted TOC **1** species was tested by the ^{1}H NMR spectroscopy which indicates the characteristic signals in the ^{1}H NMR spectral range 7.25–7.75 ppm corresponding to the “aromatic” protons of the condensed benzene rings. This fact additionally proves the presence of the magnetically-indused diatropic ring currents in the outer perimeter of the neutral hetero[8]circulenes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Bond lengths and optimized Cartesian coordinates for compounds **1–7** and for their ions, NICS indexes for the neutral circulenes **1–7** and for their ions, Mulliken charge distribution for the ground singlet state of $\mathbf{3}^{1-}$ and $\mathbf{3}^{2-}$ ions, ring-current densities and ring-current strengths in hetero[8]circulenes **4–7**. See DOI: 10.1039/b000000x/

‡ The hetero[8]circulenes family includes already synthesized tetraoxa[8]circulenes, azaoxa[8]circulenes, thio[8]circulenes and numerous theoretically predicted hetero[8]circulenes, containing different types of heteroatoms and groups (B, N, P, As, BF_2, AlF_2, GaF_2 etc.)

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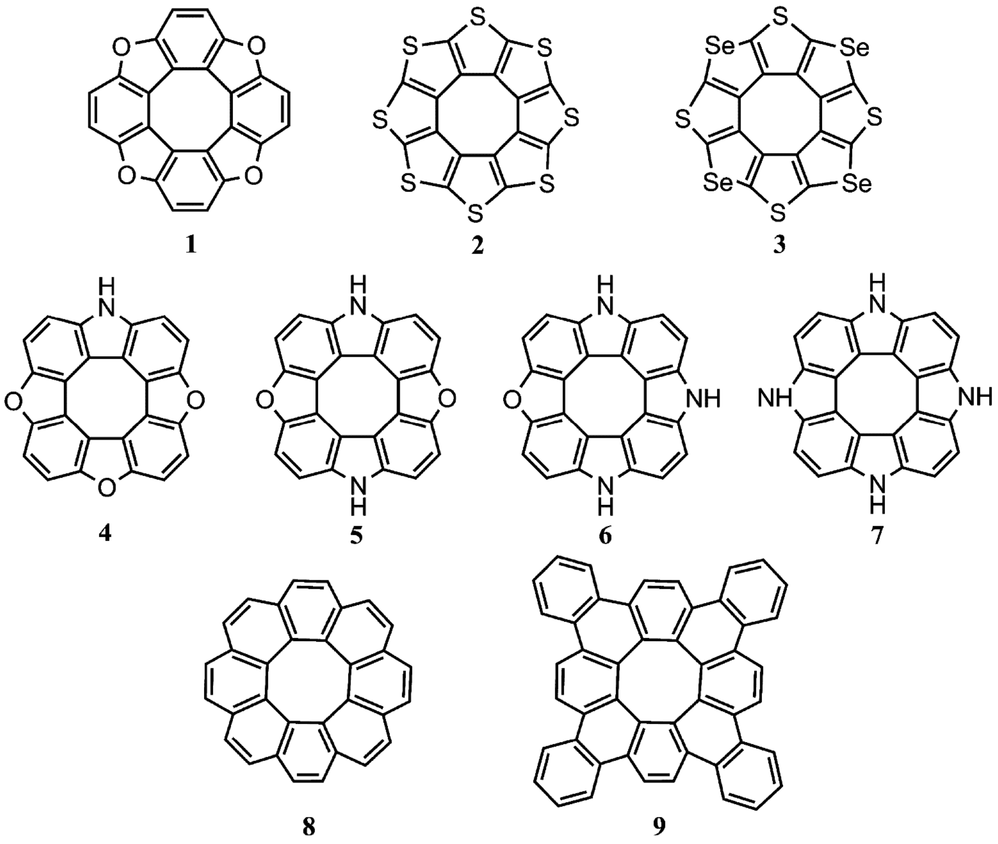


Fig. 1. Molecular structures of the series hetero[8]circulenes 1–7.
985x832mm (96 x 96 DPI)

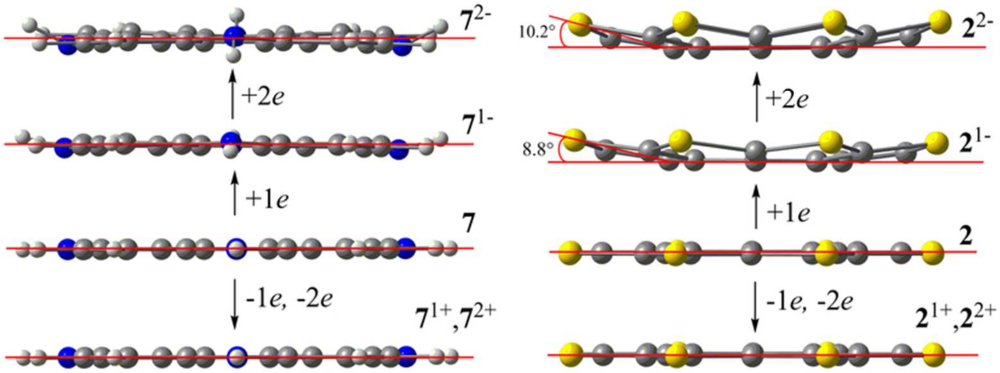
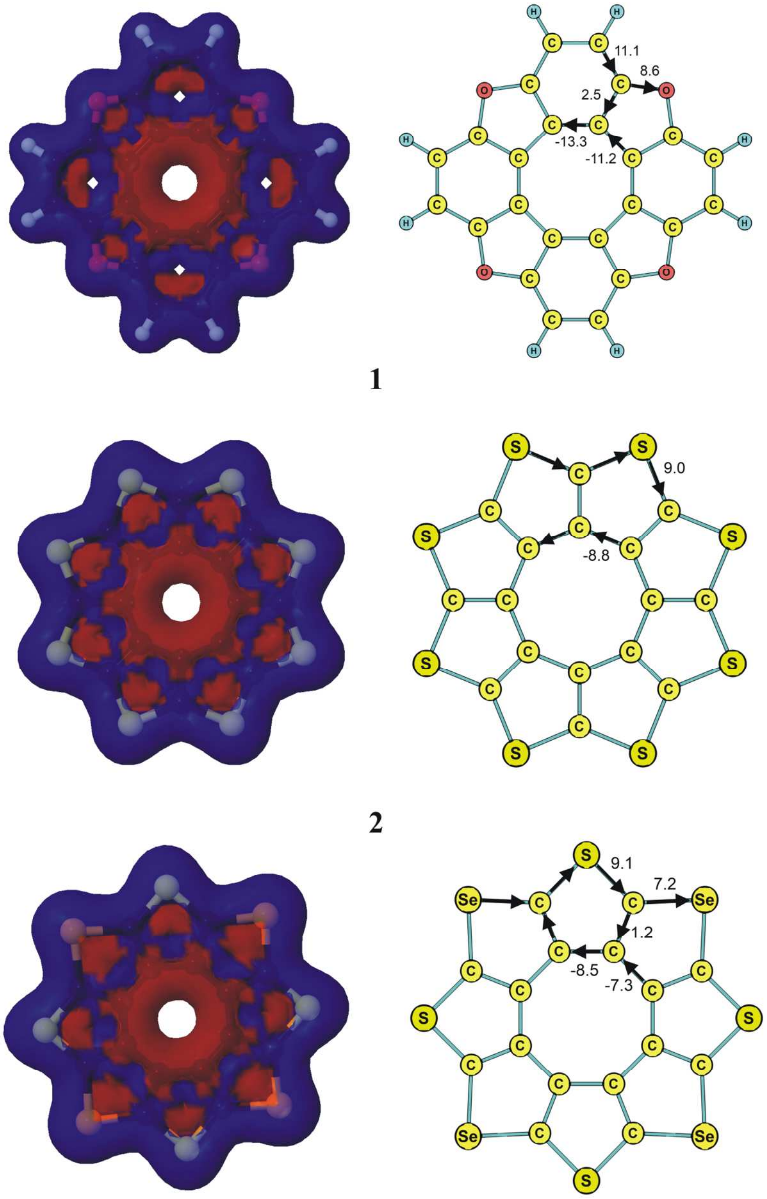


Fig. 2. The change of molecular structure for the compounds 2 (right side) an 7 (left side) upon the reduction and oxidation processes.
69x26mm (300 x 300 DPI)



1

2

Fig. 3. The ring-current densities (left) and ring-current strengths (right, nA·T−1) for each bond in the hetero[8]circulenes 1–3 molecules (red and blue colours denote the paratropic and diatropic ring currents, respectively). For the compounds 4–7 see ESI† (Fig. S4).
149x224mm (300 x 300 DPI)

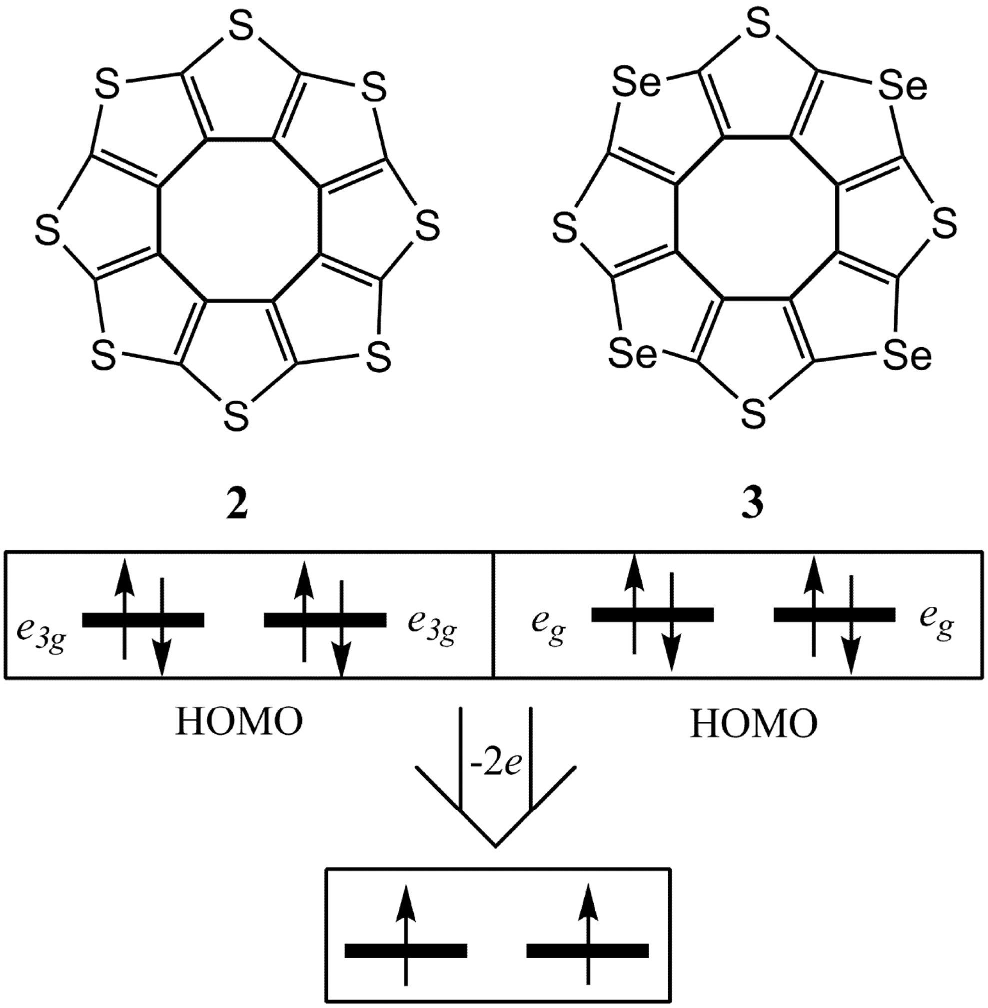
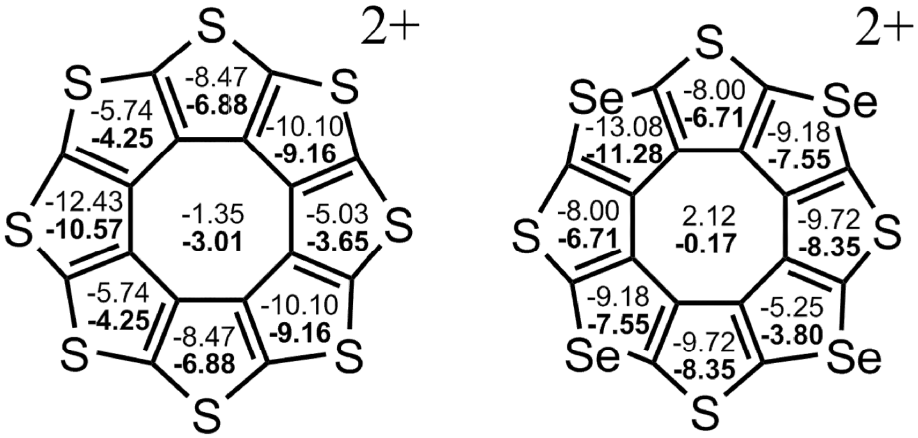
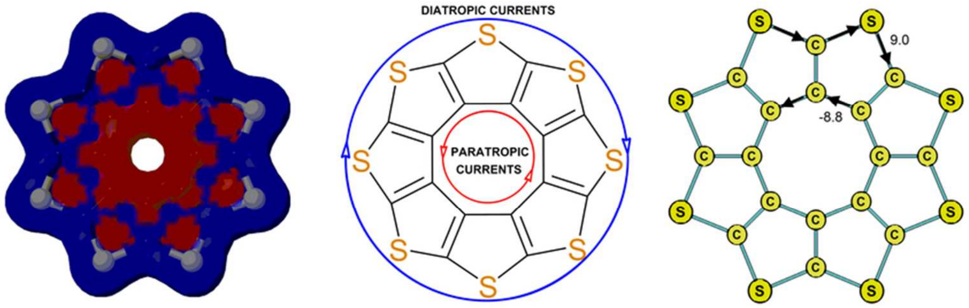


Fig. 4. Formation of the triplet state dications of compounds 2 and 3 upon double oxidation process.



2 **3**

Fig. 5. NICS(0) (top number) and NICS(1) (bottom number in bold) indexes, calculated for the triplet state dications of compounds 2 and 3.
1611x954mm (96 x 96 DPI)



all hetero[8]circulenes represent nonaromatic species because the paratropic internal currents (red colour) substantially cancel out the diatropic contribution on the outside edge (blue colour)
73x22mm (300 x 300 DPI)