PCCP

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Aromaticity of the doubly charged [8]circulenes

Gleb V. Baryshnikov,[a,b] Rashid R. Valiev,[c,d] Nataliya N. Karaush,[b]

Dage Sundholm,[e] Boris F. Minaev [b,f]

[a] *Division of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, 10691 Stockholm, Sweden*

[b] *Department of Organic Chemistry, Bohdan Khmelnitsky National University, blvd. Shevchenko 81, 18031, Cherkasy, Ukraine*

[c] *Tomsk Polytechnic University, 30 Lenin Avenue, 634050, Tomsk, Russia*

[d] *Tomsk State University, 36 Lenin Avenue, 634050, Tomsk, Russia*

[e] *Department of Chemistry, University of Helsinki, P.O. Box 55 (A.I. Virtanens plats 1), Helsinki FIN-00014, Finland*

[f] *Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Science, 100190 Beijing, China*

** Corresponding author. Tel.: +38 0472 376576; fax: +38 0472 354463.*

E-mail address: glebchem@rambler.ru (Gleb Baryshnikov)

Abstract

Magnetically induced current densities and current pathways have been calculated for a series of fully annelated dicationic and dianionic tetraphenylenes, which are also named [8]circulenes. The gauge including magnetically induced current (GIMIC) method has been employed for calculating the current density susceptibilities. The aromatic character and current pathways are deduced from the calculated current density susceptibilities showing that the neutral [8]circulenes have a two concentric pathways with aromatic and antiaromatic character, respectively. The inner octatetraene core (the hub) is found to sustain a paratropic (antiaromatic) ring current, whereas the ring current along the outer part of the macrocycle (the rim) is diatropic (aromatic). The neutral [8]circulenes can be considered nonaromatic, because the sum of the ring-current strengths of the hub and the rim almost vanishes. The aromatic character of the doubly charged [8]circulenes is completely different: the dianionic [8]circulenes and the OC-, CH-, CH_2-, SiH-, GeH-, SiH_2-, GeH_2-containing dicationic species sustain net diatropic ring currents *i.e.*, they are aromatic, whereas the O-, S-, Se-, NH-, PH- and

1

AsH-containing dicationic [8]circulenes are strongly antiaromatic. The present study also shows that GIMIC calculations on the [8]circulenes provide more accurate information about the aromatic character than obtained using local indexes such as nuclear-independent chemical shifts (NICS) and ^{1}H NMR chemical shifts.

Graphical Abstract
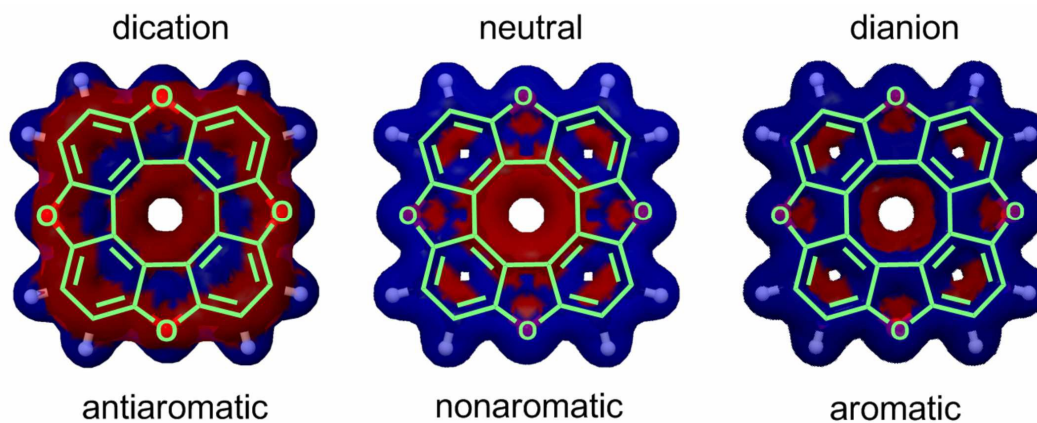
1. Introduction

Aromaticity is one of the most important and controversial concepts in chemistry characterizing physical properties and chemical reactivity of chemical compounds.[1,2] Aromaticity is a complicated property due to its multidimensional character *i.e.*, different means to assess the degree of aromaticity might lead to various results. In addition, aromaticity cannot be obtained directly from experiment, even though it is commonly used for understanding chemical properties.[2–5] Many different approaches have been proposed for assessing and quantification the degree of aromaticity of entire molecules or of parts of molecules.[1,2, 6–8] The most popular ways to determine the degree of aromaticity are structural, energetic and magnetic criteria. Nucleus-independent chemical shift (NICS)[8] calculations represent the most widely used magnetic criterion for evaluating aromaticity. NICS values are the magnetic shieldings with opposite sign calculated in selected points near the molecule under consideration. NICS values are a local indicator of the strength of the ring current circling around the studied molecular ring; NICS provides qualitative information about the aromaticity, antiaromaticity or nonaromaticity of monocyclic system like benzene, cyclobutadiene, cyclooctatetraene, furan, pyrrole etc.[8] However, the NICS approach cannot be employed for assessing the aromatic character of more complicated molecules,[9, 10] which has previously been discussed in a number of studies of the aromatic character of polycyclic aromatic hydrocarbons,[11,12] porphyrins,[13] all-metal aromatic compounds[14–18] and hydrogen-bonded molecular clusters.[19]

A more direct approach to evaluate the aromatic or antiaromatic nature of molecules as a whole is to use the gauge-including magnetically induced currents (GIMIC) method.[20–26] The GIMIC approach employs gauge-including atomic orbitals (GIAOs) in explicit calculations of the magnetically induced current density susceptibilities, current strengths and current pathways in molecules providing detailed information about electronic delocalization properties. Some interesting examples of GIMIC applications are current density studies on fullerene C_{60} and its multicharged C_{60}^{10+} ion,[27] [n]cycloparaphenylenes,[28] nano-sized hydrocarbons[29] etc.

The aromaticity concept has recently been applied to a wide variety of conjugated polyheterocyclic compounds in order to understand their chemical properties.[30–34] Among them, hetero[8]circulenes possess a prominent place due to their peculiar electronic structure,[35–42] symmetry,[40,43,44] self-assembling possibilities [45–49] and specific aromatic properties.[50–53] Moreover, they also show promise as a nanophotonic and microelectronic platform for fabrication of organic light-emitting diodes (OLEDs).[54–57] The aromatic nature of this class of compounds has been extensively studied using the structural, energetic, electronic and magnetic criteria.[40-44, 51-53] Recently,[53] we reported computational studies of the aromatic properties for a series of neutral hetero[8]circulenes **1–7** and their hydrocarbon analogues **8**, **9** shown in Figure 1.

In our previous study, we found that the [8]circulenes **1–9** are almost nonaromatic molecules (except compound **8**), because the inner paratropic ring current is only slightly larger than the diatropic ring current flowing mainly along the outer part of the molecule leading to a practically vanishing total ring-current strength.[53] The aromaticity of the novel Si- and Ge-containing [8]circulenes **10–13** (Figure 1) is investigated for the first time in this work.
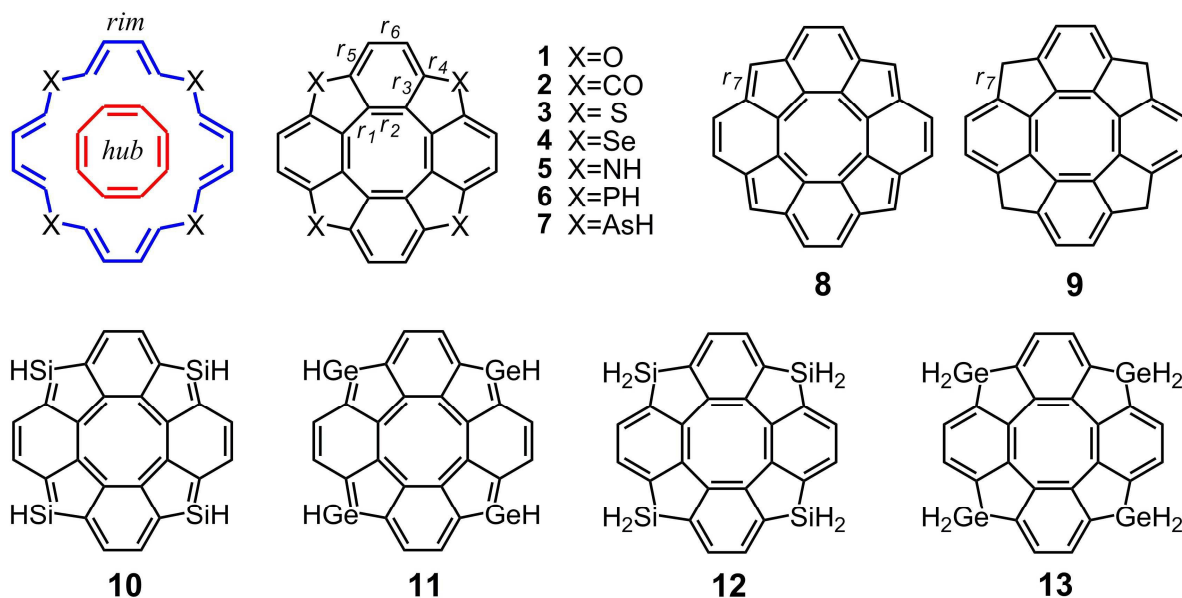
Figure 1. The molecular structures of the [8]circulenes **1–13**.

In the present work, GIMIC calculations are employed for characterizing the aromaticity of the doubly charged [8]circulenes and the obtained results are compared

with the degree of aromaticity deduced from NICS and proton nuclear magnetic resonance (^{1}H NMR) calculations.

2. Computational methods

The ground-state geometries of the examined species were optimized at the density functional theory (DFT) level employing the B3LYP [59,60] functional and the 6-311++G(d,p) basis set. [61] The GAUSSIAN 09 package was used. [62] Hessian calculations indicate that the obtained geometries of the studied species correspond to genuine minima on the potential energy surfaces at the employed level of theory.

NICS indexes [8, 63–66] were calculated at the same level of theory employing gauge-including atomic orbitals (GIAO). [67, 68] The NICS values were calculated at ghost atoms located at the center of each ring (denoted NICS(0)) and at a distance of 1 Å above the ring center (NICS(1)). The NICS(1) values were not calculated for the non-planar species. NICS(1) indexes are commonly used for better accounting for the magnetic π-electron effects [65, 66] while NICS(0) indices are considered for evaluating the sum of the σ- and π-electron delocalization effects.

Negative NICS values indicate that the molecule sustains a diatropic ring current, *i.e.,* the ring is aromatic; positive NICS values correspond to paratropic ring currents, *i.e.,* the ring is antiaromatic. [69] When the NICS value is close to zero, the ring is nonaromatic.

Magnetically induced current density susceptibilities were calculated using the GIMIC method. [20–24, 70, 71] Nuclear magnetic resonance (NMR) shielding calculations that are needed for the GIMIC calculations of the current-density susceptibilities and the ring-current susceptibilities, which are also called current densities and ring-current strengths (in nA T^{-1}), were performed using the Turbomole software package. [72] The calculated ring-current strengths can be used as an aromaticity index. For example, the current strength of the aromatic benzene molecule is 11.8 nA T^{-1} at the B3LYP/TZVP level as compared with -19.9 nA T^{-1} for the antiaromatic cyclobutadiene and 0.2 nA T^{-1} for the nonaromatic cyclohexane. [22] The current density plots have been generated using the JMOL package. [73]

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

3. Results and discussion

3.1. Molecular structures

Bond lengths of the optimized structures for the doubly charged [8]circulenes **1–13** and for the novel neutral species **10–13** are given in Table 1. The studied O-, N-, CO- and CH-containing neutral [8]circulenes are planar with a strong bond-length alternation in the inner cyclooctatetraene (COT) core. It should be noted, that the O-, N- and CO-containing circulenes **1, 2, 5** possess the highest possible D_{4h} symmetry point group, while the CH-containing compound **8** was designed with the D_{2h} symmetry in accordance with the experimental X-ray data for this species.[74,75] The more symmetrical form of compound **8** (within D_{4h} symmetry) also has a minimum on the potential energy surface. In the framework of DFT/B3LYP/6-311++G(d,p) approach both D_{2h} and D_{4h} species are degenerate by the total energy values, whereas the spin-flip (SF) DFT approach indicated that the D_{4h} form has a higher energy (34.7 kJmol^{-1} at the SF-TD-BHHLYP/6-311G(d,p) level of approximation) than D_{2h} model.[74] Moreover, Tobe at. al. found that the D_{2h} structure possess the almost closed-shell electronic structure (with very small diradical mixture) while the D_{4h} structure has the tatraradical character. On this basis, Tobe at. al. suggests that the lower symmetry D_{2h} structure may equilibrate by valence tautomerization via the D_{4h} isomer as a transition state.[74,75]

The other [8]circulenes (except **9**) possess nonplanar saddle-shaped structures due to the sectorial excess of the macrocycle in accordance with the Winberg-Dopper sectorial model.[76] The Winberg-Dopper sectorial model is described in detail in paragraph II.1 of Ref.[40] The pure hydrocarbon compound **9** has a planar tetraphenylene skeleton except for the outer nonplanar CH_2 moieties, whose hydrogens break the ideal flat structure.

The doubly charged [8]circulenes retain the molecular shape of the neutral molecules except the imidogen-containing compound **5**, whose N-H moieties deviate

out-of-plane for the dianion. The doubly charged *tetra*-hetero[8]circulenes **3**, **4**, **6**, and **7** are very nonplaner due to the increase in the C–X distances as compared with the same bond lengths of the neutral molecules. The dicationic circulene **2²⁺** and dianionic hydrocarbon-type [8]circulene **9²⁻** lack bond-length alternation in the inner eight-membered ring, whose C–C bond lengths of 1.444 Å and 1.448 Å are practically equal suggesting that the aromatic nature of the COT core is similar to that of octathia[8]circulene and its dianion.[52]

Table 1. Selected bond lengths (in Å) of the singlet ground state of the doubly-charged fully annelated tetraphenylenes **1 – 13** calculated at the B3LYP/6-311++G(d,p) level.

Circulene	Symmetry	r_1 (CC long)	r_2 (CC short)	R_3 (CC radial)	r_4 (CX)	r_5 (CC side)	r_6 (CC top)	r_7 (CC side)*
1²⁺	D_{4h}	1.435	1.384	1.416	1.369	1.384	1.425	–
1²⁻	D_{4h}	1.421	1.406	1.418	1.399	1.379	1.447	–
2²⁺	D_{4h}	1.444	1.444	1.436	1.200	1.369	1.421	1.490
2²⁻	D_{4h}	1.489	1.387	1.435	1.247	1.399	1.385	1.461
3²⁺	D_{2d}	1.485	1.409	1.445	1.729	1.384	1.392	–
3²⁻	D_{2d}	1.467	1.440	1.448	1.762	1.374	1.410	–
4²⁺	D_{2d}	1.484	1.407	1.443	1.879	1.382	1.399	–
4²⁻	D_{2d}	1.469	1.437	1.446	1.909	1.372	1.413	–
5²⁺	D_{4h}	1.473	1.368	1.429	1.375	1.405	1.385	–
5²⁻	C_s	1.430	1.421	1.426	1.401	1.392	1.415	–
6²⁺	D_{2d}	1.466	1.418	1.441	1.823	1.377	1.412	–
6²⁻	D_{2d}	1.461	1.444	1.448	1.823	1.373	1.417	–
7²⁺	D_{2d}	1.467	1.421	1.438	1.959	1.373	1.417	–
7²⁻	D_{2d}	1.464	1.443	1.446	1.947	1.371	1.420	–
8	D_{2h}	1.483	1.384	1.435	–	1.389	1.400	1.450
8²⁺	C_2	1.479	1.360	1.455	–	1.409	1.384	1.409
8²⁻	C_{2h}	1.491	1.388	1.457	–	1.418	1.378	1.407
9	D_{2d}	1.488	1.412	1.418	-	1.386	1.389	1.498
9²⁺	D_{2d}	1.462	1.432	1.436	–	1.373	1.409	1.490
9²⁻	D_{2d}	1.448	1.448	1.441	–	1.372	1.427	1.506
10	C_2	1.499 1.517	1.391 1.403	1.442 1.459 1.466	1.801, 1.760 1.854, 1.812	1.396, 1.394 1.416, 1.419	1.394 1.365	–
10²⁺	D_{2d}	1.513	1.390	1.454	1.701, 1.791	1.401	1.390	
10²⁻	C_2	1.516	1.410 1.408	1.441 1.444	1.855, 1.859	1.396 1.401	1.383 1.390	–
11	C_2	1.499 1.520	1.401 1.400	1.440 1.438 1.448	1.859, 1.867 1.964, 1.959	1.400, 1.396 1.402, 1.405	1.381 1.378	–
11²⁺	D_{2d}	1.513	1.394	1.439 1.447	1.873	1.398	1.382	–
11²⁻	C_2	1.515	1.409 1.411	1.435 1.436	1.957 1.963	1.392 1.396	1.387 1.386	–

12	D_{2d}	1.514	1.413	1.429	1.863	1.388	1.389	–
12^{2+}	D_{2d}	1.457	1.434	1.444	1.887	1.373	1.422	–
12^{2-}	D_{2d}	1.507	1.407	1.446	1.837	1.405	1.380	–
13	D_{2d}	1.513	1.415	1.425	1.945	1.387	1.391	–
13^{2+}	D_{2d}	1.460	1.434	1.440	1.967	1.372	1.423	–
13^{2-}	D_{2d}	1.463	1.447	1.451	1.935	1.374	1.421	–

X denotes heteroatoms. The bond lengths of the outer side of the five-membered hydrocarbon ring in molecules **2**, **8**, **9** are indicated with an asterisk (*).

The geometry optimizations at the DFT level yielded nonplanar molecular structures for the novel hetero[8]circulenes **10**–**13** (Figure 1). The molecular structures belong to the C_2 point group for circulenes **10** and **11** and to D_{2d} for **12** and **13**. The reason for the low symmetry of the neutral circulenes **10** and **11** and for their dianions is the two sp^3-hybridized silicon and germanium atoms. Similar distortions of the molecular structure upon reduction have previously been reported for tetraza[8]circulene **5**.[52] The doubly oxidized circulene dications **10^{2+}** and **11^{2+}** have high symmetry, belonging to the D_{2d} point group.

The novel [8]circulenes **10**–**13** have a strong bond-length alternation of the C–C bonds in the inner COT core with variations of 0.098–0.120 Å in the bond lengths, which can be compared with 0.136 Å for the strongly antiaromatic free COT that also possesses D_{2d} symmetry.[40] The bond lengths are given in Table 1. The bond-length alternation of the COT bonds in the inner COT core of dianionic and dicationic molecules does not exceed 0.026 Å, except for **12^{2-}**, whose bond-length alternation is 0.1 Å. The small bond-length alternation indicates that the doubly charged molecules are more aromatic than the neutral ones. However, it is the well known, that equal bond lengths cannot be used as the only criterion for aromaticity, because some molecules with almost equal bond lengths are not aromatic, as discussed in Ref.[65]. Other criteria characterizing the aromaticity such as chemical reactivity and energetic criteria have also some limitations, whereas magnetic properties such as ^{1}H NMR chemical shifts, magnetic susceptibility exaltation, NICS and GIMIC indexes, etc. are perhaps more reliable than the classical criteria. They are therefore the most often used means for

characterizing aromatic and antiaromatic compounds. In the next section, we discuss aromatic characters obtained using GIMIC, NICS and ^{1}H NMR calculations.

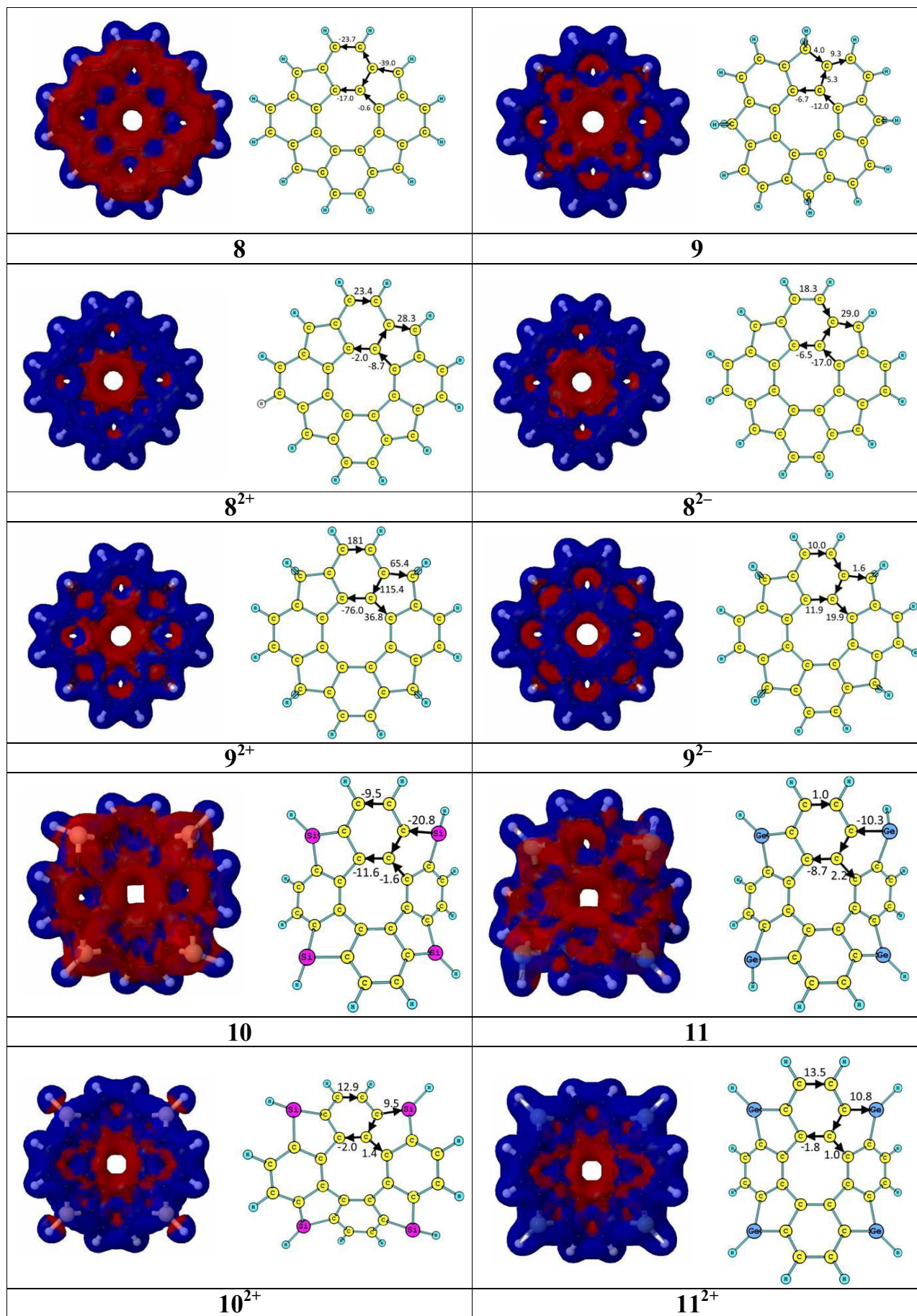### 3.2. GIMIC studies of the neutral [8]circulenes 8–13.

The signed modulus plots of the calculated magnetically induced current densities, current pathways and current strengths for the neutral [8]circulenes **8-13** are shown in Figure 2. Current density data are given for the neutral and the corresponding charged molecules. The aromatic character of the neutral [8]circulenes **8** and **9** has been previously discussed in Refs.[52,53]. The calculated current strengths circling around the macrocycle of the neutral and doubly charged tetraphenylenes **1**–**13** are summarized in Table 2, which also reports how the net diatropic (aromatic) and paratropic (antiaromatic) ring currents of the studied molecules depend on the molecular charge.

Table 2. The total ring current strength (in nA T^{-1}) and the balance between the diatropic (d) and paratropic (p) currents in the *rim*- and *hub*-subsystems for the neutral and doubly charged tetraphenylenes **1**–**13**.

| Species | Current | | | Total current strength, nA T^{-1} | Conclusion | Source |
	rim-system	*hub*-system	balance			
1	d	p	p > d	−2.1	Weakly antiaromatic	Ref.[52]
1^{2+}	p	d	p > d	−55	Antiaromatic	This work
1$^{2−}$	d	d	2d	22	Aromatic	This work
2	d	p	p > d	−4	Weakly antiaromatic	Ref.[51]
2^{2+}	d	d	2d	12	Aromatic	This work
2$^{2−}$	d	p	d > p	7.8	Aromatic	This work
3	d	p	d ≈ p	−1	Almost nonaromatic	Ref.[51]
3^{2+}	p	d	p > d	−84	Strongly antiaromatic	This work
3$^{2−}$	d	d	2d	19.5	Aromatic	This work
4	d	p	d ≈ p	−1	Almost nonaromatic	Ref.[51]
4^{2+}	p	d	p > d	−74	Strongly antiaromatic	This work
4$^{2−}$	d	d	2d	17.3	Aromatic	This work
5	d	p	d ≈ p	−0.5	Almost nonaromatic	Ref.[52] (SI)
5^{2+}	d	p	p > d	−3	Weakly antiaromatic	This work
5$^{2−}$	d	d	2d	21	Aromatic	This work
6	d	p	p > d	−2.5	Weakly antiaromatic	Ref.[51]

6^{2+}	p	d	p > d	−66	Strongly antiaromatic	This work
$6^{2−}$	d	d	2d	17	Aromatic	This work
7	d	p	p > d	−4	Weakly antiaromatic	Ref.[51]
7^{2+}	p	d	p > d	−8	Antiaromatic	This work
$7^{2−}$	d	d	2d	15.4	Aromatic	This work
8	p	p	2p	−40	Strongly antiaromatic	Ref.[51]
8^{2+}	d	p	d > p	19.6	Aromatic	This work
$8^{2−}$	d	p	d > p	11.8	Aromatic	This work
9	d	p	p > d	−2.7	Weakly antiaromatic	Ref.[51]
9^{2+}	d	p	d > p	105	Strongly aromatic	This work
$9^{2−}$	d	d	2d	21.9	Aromatic	This work
10	p	p	2p	−22.4	Antiaromatic	This work
10^{2+}	d	p	d > p	10.5	Aromatic	This work
$10^{2−}$	d	p	d > p	4.0	Weakly aromatic	This work
11	p	p	2p	−8	Antiaromatic	This work
11^{2+}	d	p	d > p	11.0	Aromatic	This work
$11^{2−}$	d	p	d > p	1.8	Weakly aromatic	This work
12	d	p	d ≈ p	−0.9	Almost nonaromatic	This work
12^{2+}	d	d	2d	8.5	Aromatic	This work
$12^{2−}$	d	d	2d	14.5	Aromatic	This work
13	d	p	d ≈ p	−0.5	Almost nonaromatic	This work
13^{2+}	d	d	2d	9.0	Aromatic	This work
$13^{2−}$	d	d	2d	14.0	Aromatic	This work

In Table 2, one sees that most of the neutral [8]circulenes are practically nonaromatic, since they do not sustain any strong net ring currents around the macroring. The net ring currents vanish for **1-7,** and **9**, because the diatropic ring current in the rim and the paratropic contribution to the ring current in the hub are almost equal. In **6, 7** and **9**, the benzoic rings also sustain local ring currents. The [8]circulenes with CH, SiH and GeH moieties (**8**, **10** and **11**) are antiaromatic sustaining net paratropic (*i.e.,* negative) ring currents, whose strength decreases with increasing atomic number. The same trend is also obtained for the corresponding sp^3-hybridized CH_2-, SiH_2- and GeH_2-containing compounds (**9**, **12** and **13**). However, they sustain very weak net ring currents of -2.7 to -0.5 nA T^{-1}, implying that they are globally almost nonaromatic. In neutral **12** and **13**, the four benzoic rings are locally aromatic, whereas very weak currents pass between the aromatic benzoic rings via the five-membered rings (Figure 2).
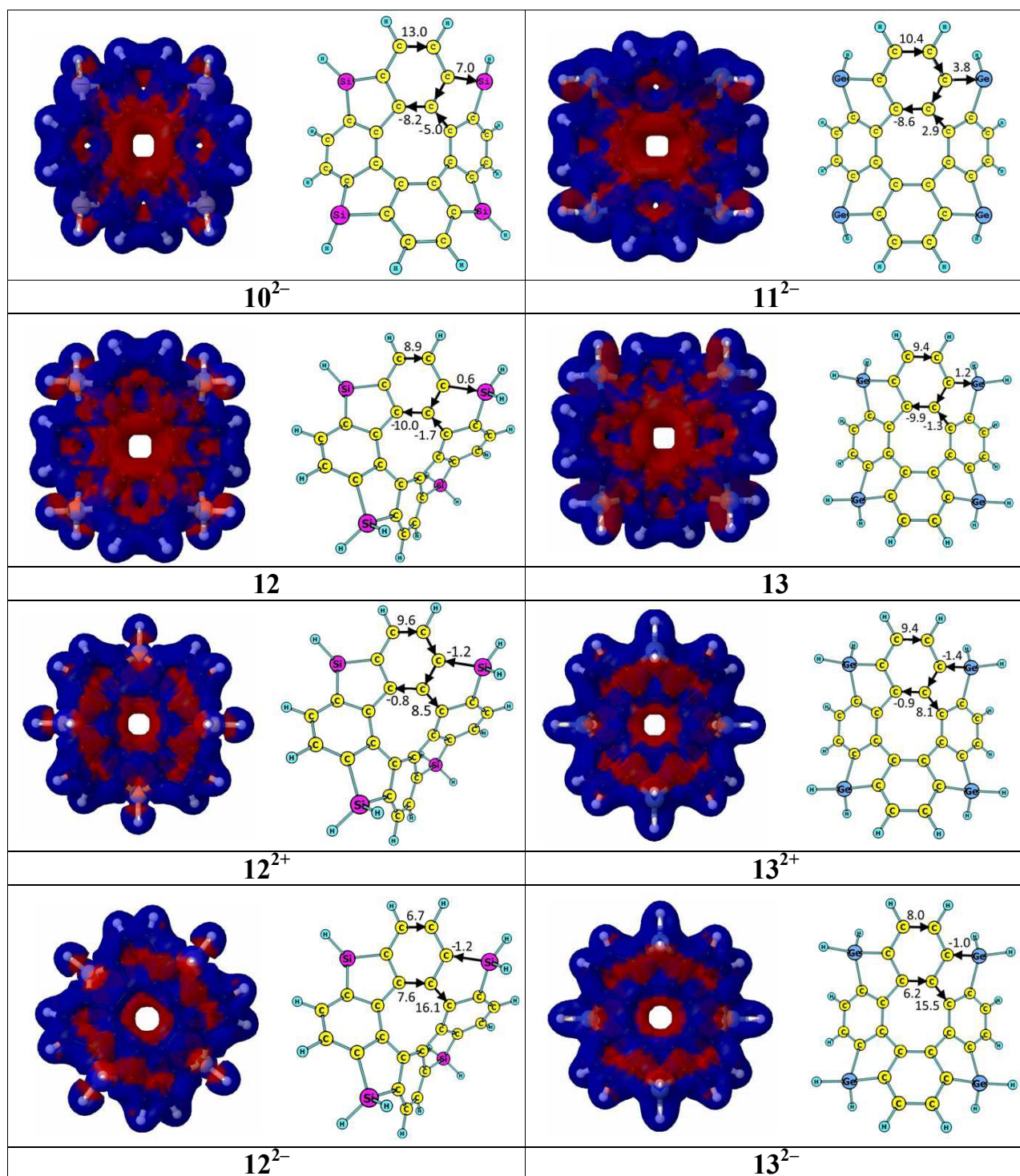
Figure 2. The signed modulus of the magnetically induced current densities, current strengths and current pathways for the neutral and doubly charged [8]circulenes **8–13**. Paratropic current densities are shown in red and the diatropic ones in blue.

3.3. GIMIC studies of the doubly charged [8]circulene anions

The aromatic nature of the doubly charged circulenes **1-13** differs completely from

that of the neutral ones. The current densities, current pathways and strengths are given in Figures 2 and 3. The ring-current strengths in Table 2 show that the dianionic species generally possess aromatic character as they sustain net diatropic ring currents. The net ring currents for the dianions are positive mainly because the ring current in the inner COT core changes direction when adding two electrons. However, the current pathways of the doubly charged anions are more complicated than that. In 1^{2-}, 3^{2-}, 4^{2-}, and 5^{2-}, the diatropic ring current pass the benzoic ring along the rim and the hub, whereas at the five-membered ring the rim current splits into an outer and inner branch of almost equal strengths. In 2^{2-}, a diatropic current flows along the rim passing the formal single bonds of the carbonyl group, whereas a weak paratropic current circles around the hub. In 6^{2-}, 7^{2-}, 9^{2-}, 12^{2-} and 13^{2-}, the outer moieties of the five-membered rings block the ring current, whereas the hub sustains a strong diatropic ring current that splits into an outer and inner route of about equal strengths at the benzoic rings. 8^{2-} sustains a diatropic ring current along the rim and a weaker paratropic one in the hub. In addition the five-membered rings sustain local ring currents. The net current for the 8^{2-} is diatropic (i.e. 8^{2-} is aromatic) in a good agreement with the suggestions of Tobe at. al. done on the basis of NISC(1) calculations.[75] 10^{2-} and 11^{2-} sustain a diatropic ring current along the rim and a weak paratropic current in the hub. The benzoic rings also sustain local ring currents. For the studied molecules, the COT core gains aromatic character when adding two electrons leading to *hub*-aromaticity or to reduced *hub*-antiaromaticity and the ring current along the outer perimeter is in most cases diatropic, which we call *rim*-aromaticity. However, for some of the doubly charged anions, the outer moieties of the five-membered rings practically block the current forcing the main ring current to take the inner route. The sum of the strengths of *hub*- and *rim*-currents yields the net ring current that determines the global aromatic character.

3.4. GIMIC studies of the doubly charged [8]circulene cations

The current pathways of the dications are even more irregular that the ones for the dianions. The current densities, current pathways and strengths are shown in Figures 2 and 3. 1^{2+} sustains a strong paratropic rim current. The benzoic rings sustain a local ring

current and a weak paratropic current passes on the inside of the five-membered ring leading to strong antiaromaticity. The ring current in 2^{2+} takes the outer route at the benzoic ring and the inner route at the five-membered rings. Almost no current passes along the hub at the benzoic rings and along the rim of the five-membered rings. 3^{2+} sustains a strong paratropic rim current and a weak diatropic hub current. The five-membered rings sustain weak local paratropic ring currents. 4^{2+} sustains a strong paratropic rim current that splits into a weak inner branch at the benzoic rings, whereas the five-membered rings sustain local paratropic ring currents. 5^{2+} sustains a diatropic rim current and a paratropic hub current of about the same size leading to a practically nonaromatic molecule. The five-membered rings sustain a weak local diatropic ring current. 6^{2+} is strongly antiaromatic with a strong paratropic rim current. Paratropic currents also pass along the inner route of the five-membered rings and the benzoic rings sustain local paratropic ring currents. 7^{2+} sustains a paratropic rim current that splits at the five-membered rings into an outer and inner branch. The benzoic rings sustain weak local paratropic ring currents. 8^{2+} is globally aromatic sustaining a strong diatropic rim current and a very weak paratropic hub current. It agrees well with the NICS(1) calculations from Ref. [75]. The five-membered rings are aromatic sustaining local diatropic ring currents. 9^{2+} is strongly aromatic sustaining a net ring current of 105 nA T^{-1}. The benzoic rings are also very aromatic with a local ring current of 76 nA T^{-1}. At the five-membered rings the diatropic rim current is split into an outer and inner branch. Two thirds of the global diatropic current passes the outer sp^3-hybridized CH_2 moiety of the five-membered rings. 10^{2+} and 11^{2+} sustain global diatropic ring currents that split into a strong outer branch and a weak inner one at the five-membered rings. The benzoic rings sustain weak local diatropic ring currents. 12^{2+} and 13^{2+} sustain global diatropic ring currents that takes the outer route at the benzoic rings and the inner pathway at the five-membered rings. Almost no net current passes the other bonds.

1^{2+}

1^{2-}

2^{2+}

2^{2-}

3^{2+}

3^{2-}

4^{2+}

4^{2-}

5^{2+}

5^{2-}
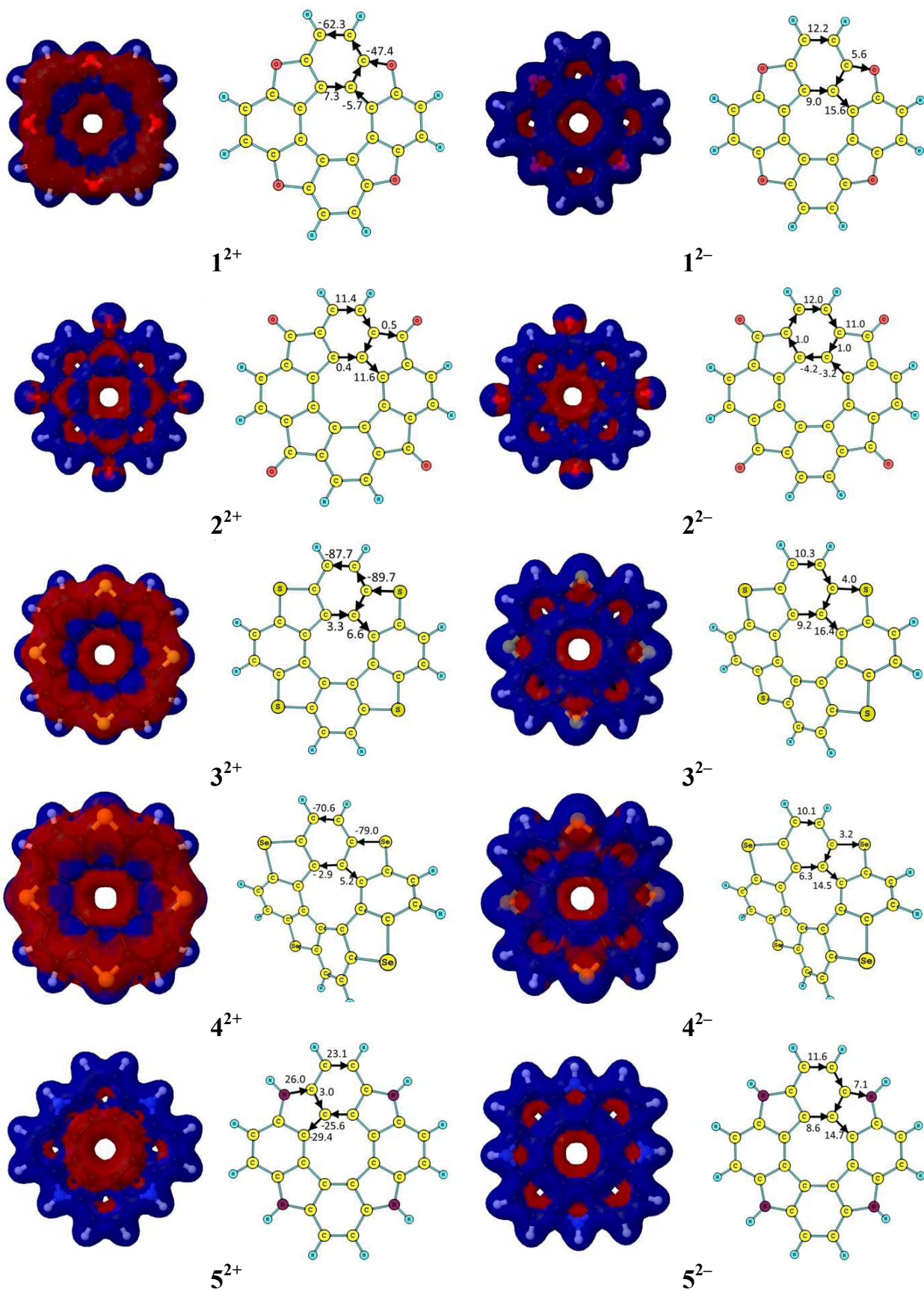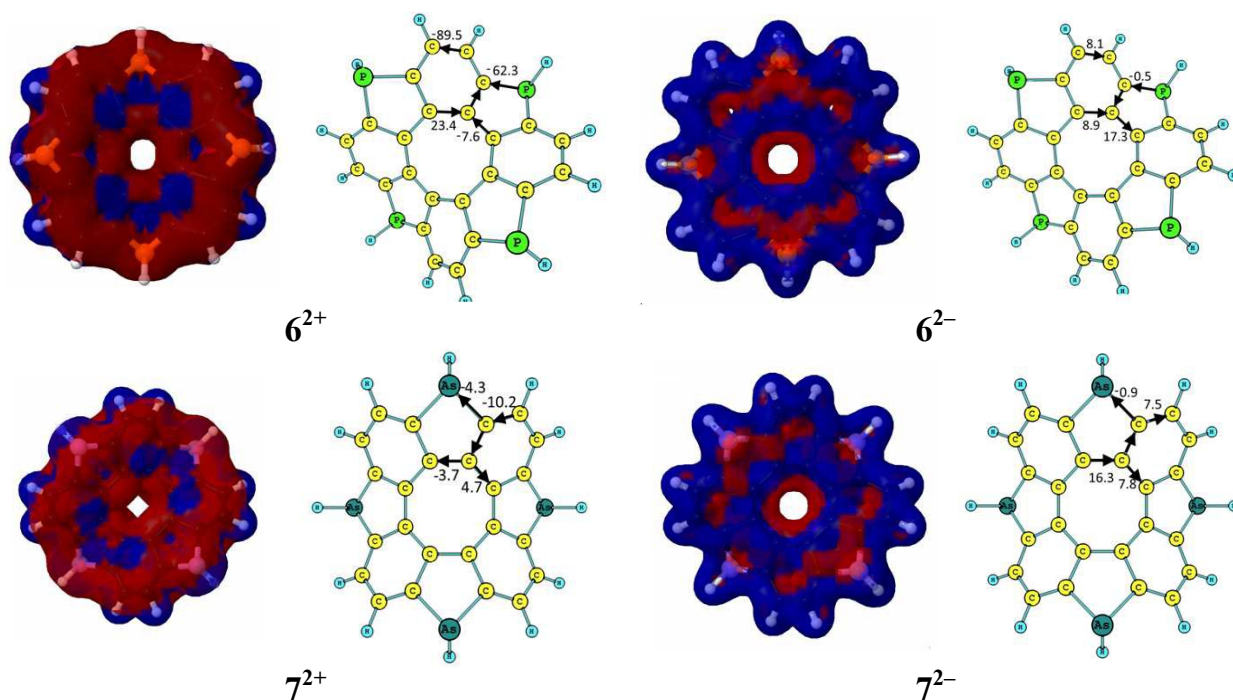
Figure 3. The signed modulus of the magnetically induced current densities, current strengths and current pathways for doubly charged [8]circulenes **1–7**. Paratropic current densities are shown in red and the diatropic ones in blue.

3.5. NICS characterization

In this section, we show that the NICS criterion cannot be employed in aromaticity studies of the [8]circulenes due to the local properties of the NICS indexes. It is almost impossible to deduce a correct analysis of the complex aromatic character of the [8]circulenes by performing NICS calculations. The main differences and similarities between the NICS- and GIMIC-based results are discussed below.

The NICS values in Figures 4 and 5 show that the dianionic [8]circulenes contain a local aromatic centre as the NICS values are negative. However, it is not apparent from the NICS calculations whether the dianionic [8]circulenes are globally aromatic or not. Only for 1^{2-}–5^{2-} and 8^{2-} the NICS indexes predict that molecules are globally aromatic *i.e.,* all the five-, six- and eight-membered rings possess local aromatic character as indicated by the negative NICS indexes for each of them. NICS calculations suggest that the rest of the dianions consist of local antiaromatic five- or eight-membered cycles. However, when one accepts the idea that the paramagnetic

contributions from these rings are significantly smaller than the diatropic ones, the NICS- and GIMIC-based results can be considered to agree with each other.
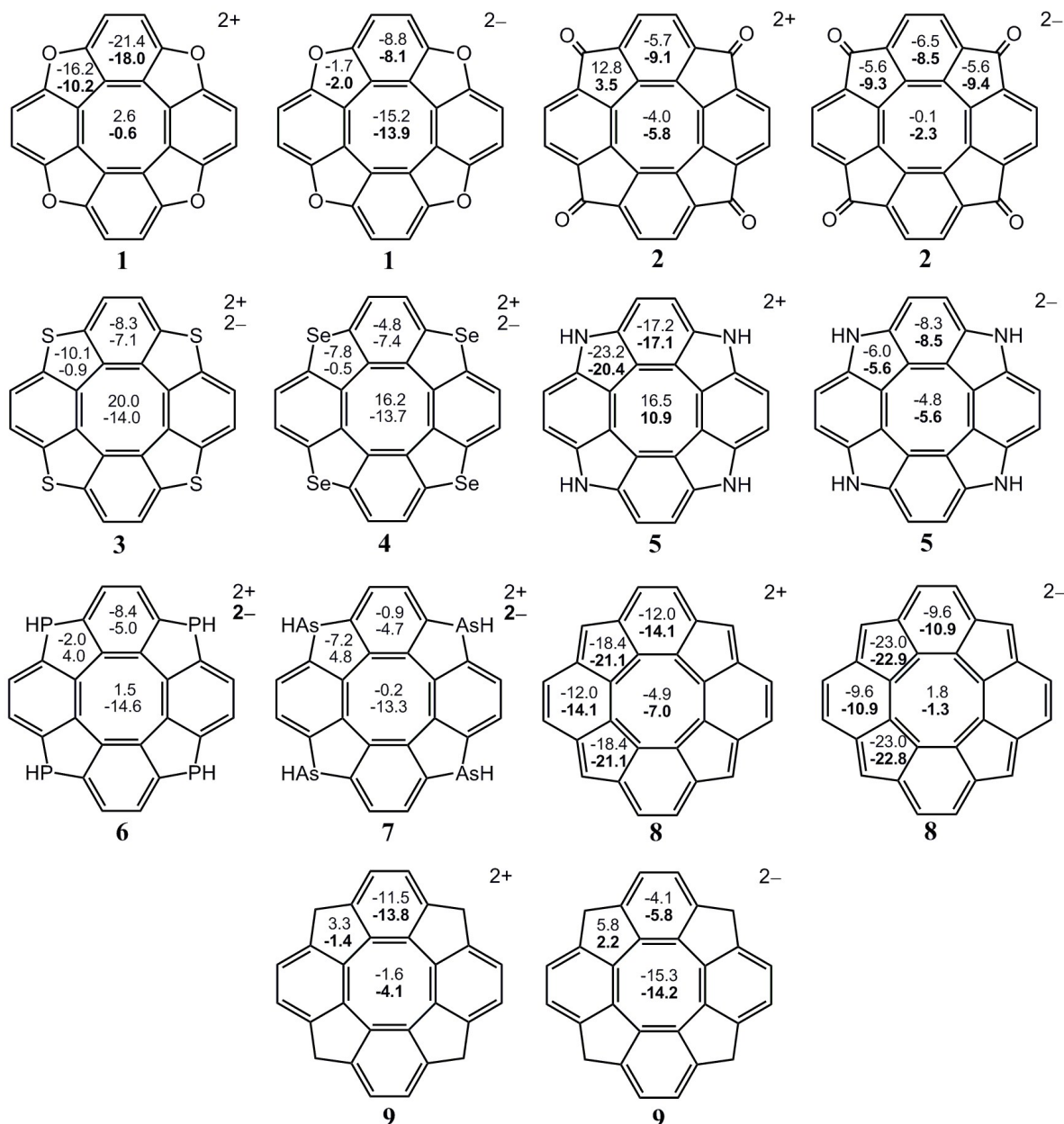

Figure 4. The NICS(0) and NICS(1) (in bold when available) indexes for the doubly charged circulenes **1–9.**

For the dicationic [8]circulenes, the NICS results agree with GIMIC data only for 8^{2+}, 10^{2+}, 11^{2+}, which are predicted to be aromatic. The NICS indexes for the other doubly oxidized species do not unambiguously provide the aromatic character as obtained in the GIMIC calculations. The NICS values have the opposite signs for the

five-, six- and eight-membered rings, as shown in Figures 4 and 5. Moreover, the analysis of the NICS indexes for the dications 1^{2+}, 5^{2+}–7^{2+} and the neutral **9**, **12**, **13** species suggests that they are aromatic rather than antiaromatic, which disagrees with the GIMIC results.
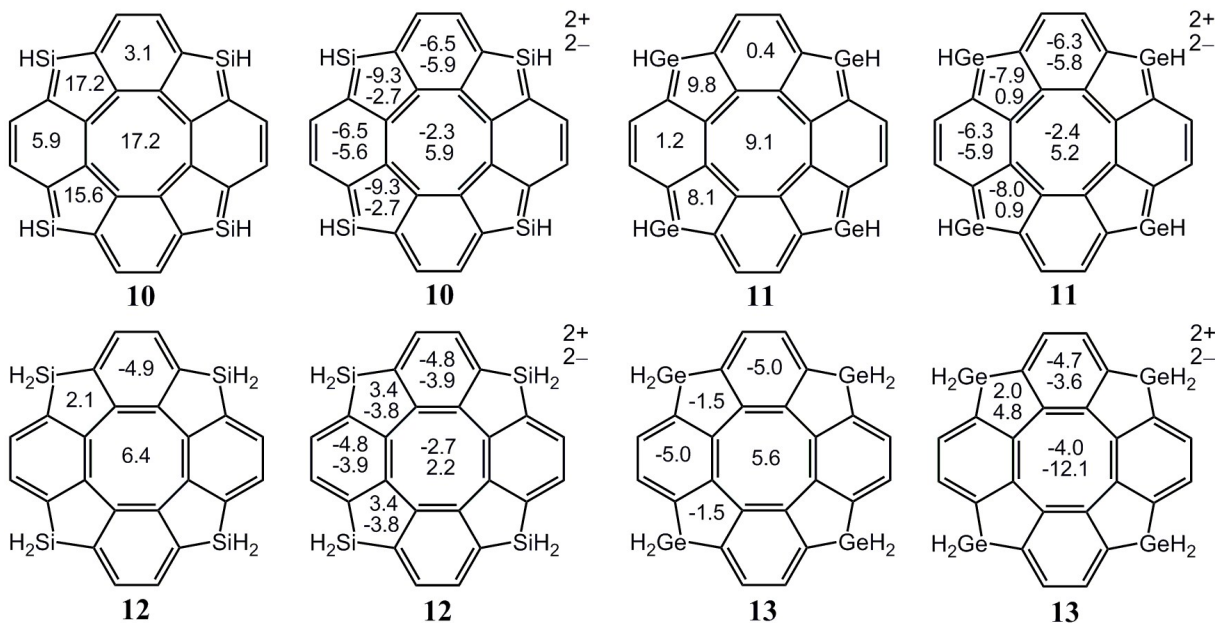
Figure 5. The NICS(0) indexes for the neutral and doubly charged [8]circulenes **10–13**.

In summary, we conclude that the NICS criterion is rather unreliable for obtaining correct description of the complex aromatic nature of the neutral and doubly charged hetero[8]circulenes due to the local character of NICS indexes. However, with the GIMIC approach one can explicitly calculate the current strength and current pathways providing an accurate and detailed picture of the ring current pathways rendering it possible to determine the aromatic character of molecules with complex annelated rings.

3.6. ^{1}H NMR chemical shift characterizations

Spectroscopic measurements of proton NMR chemical shifts (^{1}H NMR) are one of the most popular experimental methods to assess the aromaticity of polycyclic compounds. Diatropic (aromatic) ring currents deshield the protons at the outer edge of the molecule leading downfield shift of the ^{1}H NMR signal relative to the tetramethylsilane (TMS) reference. The general aromatic chemical shift region for the

protons directly connected to the aromatic framework varies in the vide range of 6.5–9 ppm and the chemical shift strongly depends on the type and position of heteroatoms in the carbon skeleton.

Table 3. Calculated and measured ^{1}H NMR chemical shifts for the studied circulenes.

Circulene	Chemical shift range (δ), ppm		
	2^+	0	2^-
1	10.89 (8CH)	7.80/7.68[a] (8CH)	6.58 (8CH)
2	10.18 (8CH)	7.72 (8CH)	8.63 ÷ 8.47 (8CH)
3	9.80 (8CH)	8.23 (8CH)	6.96 (8CH)
4	6.86 (8CH)	7.92 (8CH)	7.05 (8CH)
5	10.12 (8CH), 12.58 (4NH)	7.68 (8CH), 7.95 (4NH)	6.18 (8CH), 5.16 (4NH)
6	9.43 (8CH), 7.73 (4PH)	7.63 (8CH), 5.82 (4PH)	7.07 (8CH), 6.74 (4PH)
7	7.26 (8CH), 9.08 (4AsH)	7.32 (8CH), 5.50 (4AsH)	6.89 (8CH), 6.26 (4AsH)
8	12.03 (8CH), 13.08 (4CH)	1.24 (8CH), 0.70 (4CH) / 2.86[b]	8.78 (8CH), 9.42 (4CH)
9	10.04 (8CH), 5.67(4CH$_2$)	7.43 (8CH), 3.92 (4CH$_2$)	6.60 (8CH), 4.06 (4CH$_2$)
10	9.68 (8CH), 9.21 (4SiH)	5.25 ÷ 5.68 (4SiH), 4.91 ÷ 5.50 (8H)	7.18 ÷ 7.19 (4SiH), 7.76 ÷ 7.96 (8CH)
11	9.44 (8CH), 9.98 (4GeH)	6.12 ÷ 7.62 (4GeH), 5.99 ÷ 7.22 (8H)	7.33 (4GeH), 7.98 ÷ 7.33 (8CH)
12	5.92 ÷ 6.17 (4SiH$_2$), 8.99 (8CH)	5.20 (4SiH$_2$), 7.92 (8CH)	6.62 ÷ 6.58 (4SiH$_2$), 7.58 ÷ 7.52 (8CH)
13	6.50 ÷ 6.09 (4GeH$_2$), 8.99 ÷ 9.02 (8CH)	5.39 (4GeH$_2$), 7.89 ÷ 7.88 (8CH)	5.33 ÷ 5.35 (4GeH$_2$), 6.96 ÷ 6.89 (8CH)

[a] experimental data from Ref.[56]
[b] experimental data from Ref.[75]

Comparisons of the calculated isotropic magnetic shielding constants with the ^{1}H NMR shielding constant for TMS calculated at the same level of theory yield the calculated values for the ^{1}H NMR chemical shifts in Table 3. The calculated ^{1}H NMR chemical shifts of the hydrogens of the benzoic rings of the neutral [8]circulenes fall in the aromatic range. The exceptions are compounds **8**, **10** and **11**, which possess the *rim-*antiaromaticity implying that the corresponding NMR signals are upfield shifted, which is in a good agreement with the experimental data for compound **8**. The ^{1}H NMR chemical shifts describe correctly the rim aromaticity of the neutral species as obtained in the GIMIC calculation. For the dianionic [8]circulenes, the hydrogens of the benzoic rings are characterized by aromatic ^{1}H NMR chemical shifts values. The same also holds for the benzoic protons of the NH, PH, AsH, CH (compound **8**), SiH and GeH

containing compounds. These results are in a good agreement with the GIMIC and NICS results. For the dicationic species the aromatic character deduced from the ^{1}H NMR chemical shifts does not agree with the ones obtained in the GIMIC calculations. The chemical shifts in Table 3 show that the hydrogens of the benzoic rings and the ones at the heteroatoms are significantly deshielded, which might indicate that the molecule sustain a strong diatropic ring current along the perimeter, which is in contradiction to the GIMIC results. We conclude that the ^{1}H NMR chemical shifts criterion as well as NICS criterion for aromaticity are not able to correctly describe the aromatic character of the hetero[8]circulene dications. For the neutral and dianionic species, the ^{1}H NMR chemical shifts indexes provide a more reliable description of the aromaticity. A further limitation of the ^{1}H NMR chemical shifts criterion is that the inner COT core of the [8]circulenes does not contain any directly fused protons, which means that the criterion can not be applied for assessing the hub aromaticity.

4. Conclusions

In the present work, we have presented the structural characterisations and aromaticity descriptions of the doubly charged [8]circulenes **1-9** and the novel neutral, dicationic and dianionic circulenes **10-13**. We have used the three most popular magnetic criteria of aromaticity, namely the gauge including magnetically induced current (GIMIC) method, calculated nucleus-independent chemical shift (NICS) values and ^{1}H NMR chemical shifts to solve the posed problem. We have found that the GIMIC-based results for the studies neutral and doubly charged [8]circulenes are much more informative than the local NICS indexes and ^{1}H NMR chemical shifts, because the GIMIC approach provides very detailed information about the current pathways, which is not feasible when using the local NICS and ^{1}H NMR chemical shifts indexes.

We found that most of the studied [8]circulenes (except compounds **8**, **10** and **11**) have a bifacial aromatic/antiaromatic character in the neutral form; the inner octatetraene core (also called *hub*) sustains a paratropic (antiaromatic) ring current, whereas the ring current of the outer macrocycle (the *rim*) is diatropic (aromatic). The aromatic character changes drastically when charging the [8]circulenes; the dianionic [8]circulenes and OC-, CH-, CH_2-, SiH-, GeH-, SiH_2-, GeH_2-containing dicationic

species sustain net diatropic ring currents *i.e.,* they are aromatic, whereas O-, S-, Se-, NH-, PH- and AsH-containing dicationic compounds are strongly antiaromatic, because they are dominated by the paratropic ring currents. The present computational study of the magnetically induced current densities suggests that the experimentally observed high stability of the synthesized [8]circulenes **1–5**, **9** is due to their *rim*-aromaticity, even though they are nonaromatic. The *rim* aromaticity favours substitution reactions of the [8]circulenes **1–5**, **9**, analogously to benzoic compounds. The carbon atoms of the hub are protected against substitution reactions, because they are sp^2 hybridized without any available hydrogen atom to replace. Addition reactions to the *hub* carbons would lead to a transformation from sp^2 to sp^3 hybridization that significantly affects most of the C–C bonds of the [8]circulene, which is expected to lead to a very high reaction barrier. Compound **8** is antiaromatic suggesting that it is unstable, which is in a good agreement with experimental data.[75] The same most likely also holds for the rest of the studied [8]circulenes, which have not yet been synthesized. The GIMIC approach opens up new possibilities for studies of the electronic structure of complex polycyclic aromatic compounds like [8]circulenes.

Acknowledgments

Notes and references

Electronic Supplementary Information (ESI) available: [Cartesian coordinates and the corresponding total energy of the singlet ground state of the studied [8]circulenes **1–13**.]. See DOI: 10.1039/b000000x/

References

1. T. M. Krygowski, M. K. Cyrański, *Chem. Rev.* 2001, **101**, 1385.

2. M. K. Cyrański, *Chem. Rev.* 2005, **105**, 3773.

3. A. R. Katritzky, P. Barczynski, G. Musumarra, D. Pisano, M. Szafran, *J. Am. Chem. Soc.*, 1989, **111**, 7.

4. M. K. Cyrański, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, *J. Org. Chem.*, 2002, **67**, 1333.

5. K. Jug, A. M. Koster, *J. Phys. Org. Chem.*, 1991, **4**, 163.

6. a) R. Gershoni-Poranne, A. Stanger, *Chem. Soc. Rev.*, 2015, **44**, 6597; b) C. Foroutan-Nejad, S. Shahbazian, P. Rashidi-Ranjbar, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12630;

7. a) S. C. A. H. Pierrefixe and F. M. Bickelhaupt, *Chem. Eur. J.*, 2007, **13**, 6321 (Erratum: *Chem. Eur. J.*, 2007, **13**, 8371); b) S. C. A. H. Pierrefixe and F. M. Bickelhaupt, *J. Phys. Chem. A*, 2008, **112**, 12816.

8. P. v. R. Schleyer, C. Maerker, H. C. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.

9. Z. Badri, S. Pathak, H. Fliegl, P. Rashidi-Ranjbar, R. Bast, R. Marek, C. Foroutan-Nejad, K. Ruud, *J. Chem. Theor. Comput.*, 2013, **9**, 4789.

10. C. Foroutan-Nejad, *Theor. Chem. Acc.*, 2015, **134**, 8.

11. J. Jusélius, D. Sundholm, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3429.

12. E. Steiner P. Fowler A. Soncini L. W. Jenneskens, *Faraday Discuss.*, 2007, **135**, 309.

13. J. Jusélius, D. Sundholm, *J. Org. Chem.* 2000, **65**, 5233.

14. Y-C. Lin, J. Jusélius, D. Sundholm, *J. Chem. Phys.* 2005, **122**, 214308.

15. P. W. Fowler, R. W. A. Havenith, E. Steiner, *Chem. Phys. Lett.*, 2002, **359**, 530.

16. J. Jusélius, S. Michal, D. Sundholm, *J. Phys. Chem. A*, 2001, **105**, 9939.

17. Y-C. Lin, D. Sundholm, J. Jusélius, L-F. Cui, H-J. Zhai, L-S. Wang, *J. Phys. Chem. A*, 2006, **110**, 4244.

18. C. A. Tsipis, *Coord. Chem. Rev.*, 2005, **249**, 2740.

19. Y-C. Lin, D. Sundholm, *J. Chem. Theory Comput.*, 2006, **2**, 761.

20. H. Fliegl, S. Taubert, O. Lehtonen, D. Sundholm, *Phys. Chem. Chem. Phys.,* 2011, **13**, 20500.

21. J. Jusélius, D. Sundholm, J. Gauss, *J. Chem. Phys.,* 2004, **121**, 3952.

22. H. Fliegl, D. Sundholm, S. Taubert, J. Jusélius, W. Klopper, *J. Phys. Chem. A*, 2009, **113**, 8668.

23. H. Fliegl, N. Özcan, R. Mera-Adasme, F. Pichierri, J. Jusélius, D. Sundholm, *Mol. Phys.*, 2013, **111**, 1364.

24. R. R. Valiev, H. Fliegl, D. Sundholm, *J. Phys. Chem. A*, 2013, **117**, 9062.

25. R. R. Valiev, H. Fliegl, D. Sundholm, *J. Phys. Chem. A*, 2015, **119**, 1201.

26. R. R. Valiev, H. Fliegl, D. Sundholm, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14215.

27. M. P. Johansson, J. Jusélius, D. Sundholm *Angew. Chem. Int. Ed.***,** 2005, **44**, 1843.

28. S. Taubert, D. Sundholm, F. Pichierri, *J. Org. Chem.*, 2010, **75**, 5867.

29. S. Taubert, J. Jusélius, D. Sundholm, W. Klopper, H. Fliegl, *J. Phys. Chem. A*, 2008, **112**, 13584.

30. V. T. T. Huong, T. B. Tai, M. T. Nguyen, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14832.

31. V. T. T. Huong, H. T. Nguyen, T. B. Tai, M. T. Nguyen, *J. Phys. Chem. C*, 2013, **117**, 10175.

32. G. V. Baryshnikov, N. N. Karaush, B. F. Minaev, *Chem. Heterocyc. Comp.*, 2014, **50**, 349.

33. W. Wei, F-Q. Bai, B-H. Xia, H-B. Chen, H-X. Zhang, *Chem. Res. Chin. Univ.*, 2013, **29**, 962.

34. A. Kerim, *New J. Chem.*, 2014, **38**, 3783.

35. K. Y. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova, V. G. Nenajdenko, *Angew. Chem., Int. Ed.*, 2006, **45**, 7367.

36. B. F. Minaev, G. V. Baryshnikov, V. A. Minaeva, *Comput. Theor. Chem.*, 2011, **972**, 68.

37. N. N. Karaush, B. F. Minaev, G. V. Baryshnikov, V. A. Minaeva, *Opt. Spectroscop.*, 2014, **116**, 33.

38. T. B. Tai, V. T. T. Huong, M. T. Nguyen, *Chem. Commun.*, 2013, **49**, 11548–11550.

39. N. N. Karaush, R. R. Valiev, G. V. Baryshnikov, B. F. Minaev, H. Ågren, *Chem. Phys.*, 2015, **459**, 65.

40. G. V. Baryshnikov, B. F. Minaev, V. A. Minaeva, *Russ. Chem. Rev.*, 2015, **84**, 455.

41. T. B. Tai, H. T. T. Vu, M. T. Nguyen, *RSC Adv.*, 2015, **5**, 24167.

42. X. Xiong, C.-L. Deng, B. F. Minaev, G. V. Baryshnikov, X.-S. Peng, H. N. C. Wong, *Chem. Asian J.*, 2014, **9**, 1.

43. T. N. Gribanova, N. S. Zefirov, V. I. Minkin, *Pure Appl. Chem.*, 2010, **82**, 1011.

44. G. V. Baryshnikov, V. A. Minaeva, B. F. Minaev, N. N. Karaush, X-D Xiong, M-D. Li, D. L. Phillips, H. N. C. Wong, *Spectrochim. Acta A*, 2015, **151**, 247.

45. G. V. Baryshnikov, B. F. Minaev, N. N. Karaush, V. A. Minaeva, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6555.

46. G. V. Baryshnikov, B. F. Minaev, N. N. Karaush, V. A. Minaeva, *RSC Adv.*, 2014, **4**, 25843.

47. N. N. Karaush, G. V. Baryshnikov, B. F. Minaev, *RSC Adv.*, 2015, **5**, 24299.

48. N. N. Karaush, G. V. Baryshnikov, B. A. Minaeva, B. F. Minaev, *New J. Chem.*, 2015, **39**, 7815.

49. J. Yu, Q. Sun, Y. Kawazoe, P. Jena, *Nanoscale*, 2014, **6**, 14962.

50. S. Radenković, I. Gutman, P. Bultinck, *J. Phys. Chem. A*, 2012, **116**, 9421.

51. G. V. Baryshnikov, B. F. Minaev, M. Pittelkow, C. B. Nielsen, R. Salcedo, *J. Mol. Model.*, 2013, **19**, 847.

52. G. V. Baryshnikov, R. R. Valiev, N. N. Karaush, B. F. Minaev, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15367.

53. G. V. Baryshnikov, N. N. Karaush, R. R. Valiev, B. F. Minaev, *J. Mol. Model.*, 2015, **21**, 136.

54. C. B. Nielsen, T. Brock-Nannestad, T. K. Reenberg, P. Hammershoj, J. B. Christensen, J. W. Stouwdam, M. Pittelkow, *Chem. Eur. J.*, 2010, **16**, 13030.

55. J. Eskildsen, T. Reenberg, J. B. Christensen, *Eur. J. Org. Chem.*, 2000, **2000**, 1637.

56. T. Brock-Nannestad, C. B. Nielsen, M. Schau-Magnussen, P. Hammershoj, T. K. Reenberg, A. B. Petersen, D. Trpcevski, M. Pittelkow, *Eur. J. Org. Chem.*, 2011, **31**, 6320.

57. A. Dadvand, F. Cicoira, K. Y. Chernichenko, E. S. Balenkova, R. M. Osuna, F. Rosei, V. G. Nenajdenko, D. F. Perepichka, *Chem. Commun.*, 2008, 5354.

58. H. Erdtman, H.-E. Högberg, *Tetrahedron Lett.*, 1970, **11**, 3389.

59. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

60. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

61. R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650.

62. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, revision C.02*, Gaussian, Inc., Wallingford, CT, 2009.

63. T. K. Zywietz, H. Jiao, P. V. R. Schleyer, A. De Meijere, *J. Org. Chem.*, 1998, **63**, 3417.

64. P. R. Schleyer, *Chem Rev.*, 2001, **101**, 1115.

65. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842.

66. A. Stanger, *J. Org. Chem.*, 2006, **71**, 883.

67. K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251.

68. J. R. Cheeseman, G. W. Trucks, T. A. Keith, J. M. Frisch, *J. Chem. Phys*., 1996, **104**, 5497.

69. G. Monaco, P. W. Fowler, M. Lillington, R. Zanasi, *Angew. Chem. Int. Ed.*, 2007, **46**, 1889.

70. R. R. Valiev, H. Fliegl, D. Sundholm, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11010.

71. R. R. Valiev, V. N. Cherepanov, *Int. J. Quantum. Chem.*, 2013, **113**, 2563.

72. F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *Comput. Mol. Sci.*, 2014, **4**, 91.

73. JMOL: an open-source Java viewer for chemical structures in 3D., http://www.jmol.org

74. S. Nobusue, H. Miyoshi, A. Shimizu, I. Hisaki, K. Fukuda, M. Nakano, Y. Tobe, *Angew. Chem. Int.* Ed., 2015, **54**, 2090.

75. H. Miyoshi, S. Nobusue, A. Shimizu, Y. Tobe, *Chem. Soc. Rev.*, 2015, **44**, 6560.

76. J. H. Dopper, H. Wynberg, *J. Org. Chem.*, 1975, **40**, 1957.