Magnetically Induced Currents in [n]Cycloparaphenylenes, n = 6−11
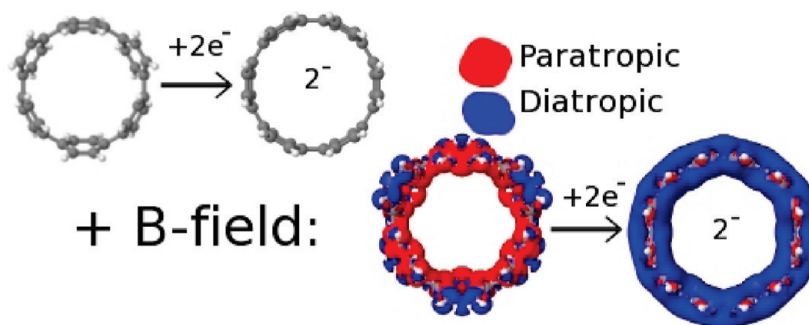
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We report calculations of the gauge-independent magnetically induced current densities in [n]cycloparaphenylenes ([n]CP), n = 6−11. In addition to the neutral [n]CPs, the dianion of [6]CP and the current densities of the corresponding metal complexes Li$_2$[6]CP and Mg[6]CP are also investigated. By the ring current criterion, the [6]CP with $4n$ π electrons has a slight antiaromatic character, while [7]CP has $(4n + 2)$ π electrons and is weakly aromatic with a ring current susceptibility strength that is about 25% of the ring current of benzene. The larger neutral [n]CPs, n = 8−11, do not sustain any net ring current around the nanohoop and are essentially nonaromatic. The weak paramagnetic ring current susceptibility of [6]CP flows along a $4n$ π pathway on either edge of the phenylene rings. For the dianions, the ring current susceptibility strengths are 24−35 nA/T diatropic and thus the addition of two electrons induces an electron delocalization and an aromatic character of the nanohoops. The dilithium complex of [6]CP with $(4n + 2)$ π electrons is aromatic with a net ring current strength of 28 nA/T or 2.4 times the ring current strength of benzene, involving all 62 π electrons in the current pathway. The ^{1}H NMR chemical shieldings and the nucleus-independent chemical shifts correlate with the strengths of the magnetically induced currents. The aromatic [n]cycloparaphenylenes have a quinoid structure, whereas the weakly aromatic or nonaromatic ones are benzoidic.

1. Introduction

Conjugated ring-shaped hydrocarbons with $(4n + 2)$ π electrons are aromatic according to Hückel's rule,[1−3] whereas the antiaromatic ones have a conjugation pathway consisting of $4n$ π electrons.[4] The electron delocalization in ring-shaped molecules and the molecular aromaticity are related[5] and the ring-current pathways in multiring molecules provide information about the extent of the electron delocalization.[6] The connection between ring-current strengths and ^{1}H NMR chemical shieldings of aromatic compounds was pointed out more than fifty years ago[7] and a direct correlation between these two entities has also been established in multiring aromatic hydrocarbons.[6] The relationship

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between ^{1}H NMR chemical shieldings and cyclic delocalization has been systematically demonstrated in a recent study.[8] Bearing the multidimensionality of the concept of aromaticity in mind,[9] the ability to sustain a net current can be considered as a necessary, although not always as a sufficient, criterion for aromaticity. A strong correlation between magnetically induced ring currents and aromatic or antiaromatic character has been shown to also exist for all-boron toroids[10] and for a series of cyclic hydrocarbons.[11] By the magnetic criterion for aromaticity, the ability to sustain a net diatropic current indicates possible aromatic character, while a net paratropic current is typical for antiaromatic molecules. Molecules that do not sustain any net ring current are considered as nonaromatic.[11]

The [n]cycloparaphenylenes ([n]CP) are hoop-shaped molecules made of 1,4-connected phenylene rings where the carbon p_π orbitals are perpendicular to the phenylene rings and are thus oriented toward the hoop's center. These esthetically appealing structures have unique physical properties, and offer the possibility of creating novel supramolecular complexes.[12−14] The [n]CPs with five and six arene rings were synthesized in 1993,[15] whereas synthesis was attempted already in 1934 by Parekh and Guha.[16] The term nanohoops was coined by Jasti and co-workers, who in 2008 synthesized [9]CP, [12]CP, and [18]CP and studied their UV−vis spectra.[17] The selective synthesis of [12]CP has subsequently been reported in 2009 by Itami's group.[18] The strain energy of nanohoops of different size has been computed at the DFT level by Segawa and co-workers.[19] The large Stokes shifts observed for the nanohoops have been suggested to arise from the confinement of the excitons to the phenylene rings in the larger [n]CPs.[20,21] Extending the nanohoop concept to metals, silver nanohoop-based materials with negative refraction index have been proposed as metamaterials for optical security.[22]

We have recently shown that the bond length alternation of the [n]CPs changes upon excitations.[21] Since bond length alternation has consequences for the ability to sustain a ring current, it is of interest to map the current density pathways in these molecules.

In this paper, we describe the magnetically induced current susceptibility densities and the ring current susceptibility strengths in the $n = 6-11$ [n]cycloparaphenylenes at the DFT level. The unit for the current susceptibility is nA/T and the

results are thus independent of the magnetic field strength. Below, the term "current susceptibility" is replaced by the shorter "current". An important aspect that we wish to address here concerns the aromatic/antiaromatic character of [n]CPs as a function of ring size and the possible differences in their electronic structures with respect to the odd/even series. Dianions are also included in this study along with the corresponding complexes with metal cations. To the best of our knowledge, few theoretical studies have been devoted to [n]CPs. Besides a DFT study on $n = 9, 12, 18$,[17] Jagadeesh et al. investigated [n]CPs, $n = 5, 6$, using semiempirical, Hartree−Fock, and DFT methods and predicted [5]CP possessing a quinoid structure while [6]CP was suggested to have a benzoid character.[23]

We have used the GIMIC method[24] to investigate the ring current strengths and ring current density distributions. The GIMIC method has previously been employed to determine the current strengths and current pathways of complex organic and inorganic species.[6,10,11,24−30] It has proven to be a useful tool for determining the degree of aromaticity of multiring molecules because it explicitly provides the strength of the magnetically induced current passing through selected chemical bonds and the strength of the currents circling around molecular rings.

2. Results and Discussion

2.1. Molecular Structures. 2.1.1. The Neutral [n]CPs. The optimized structures of the neutral nanohoops are shown in Figure 1. In all the neutral [n]CPs, $n = 6-11$, the optimized bond lengths of the corresponding bonds are equal within less than 1 pm. The C−C bond bridging two phenylene rings is 148 pm and the bonds in the phenylene rings are 139 and 141 pm, the shorter bonds being the ones at the upper and lower edge. Thus, the studied [n]CPs can be considered to mainly consist of benzenoid arene rings connected by single bonds. The optimized bond lengths in benzene are 139.1 pm at the same computational level.

The phenylene rings in the neutral nanohoops are in a staggered arrangement: every second ring is tilted inward and every second outward. The torsional angle between the phenylene rings varies between 13° and 40°. In biphenyl, the corresponding angle is 44.4°.[31,32] The torsional angles of the phenylene rings differ from the planar 180° by 7−15°.

Some of the [n]CPs with less than ten phenylene rings are highly symmetric, while the increased flexibility of the largest nanohoops yields a decreased symmetry. The symmetry

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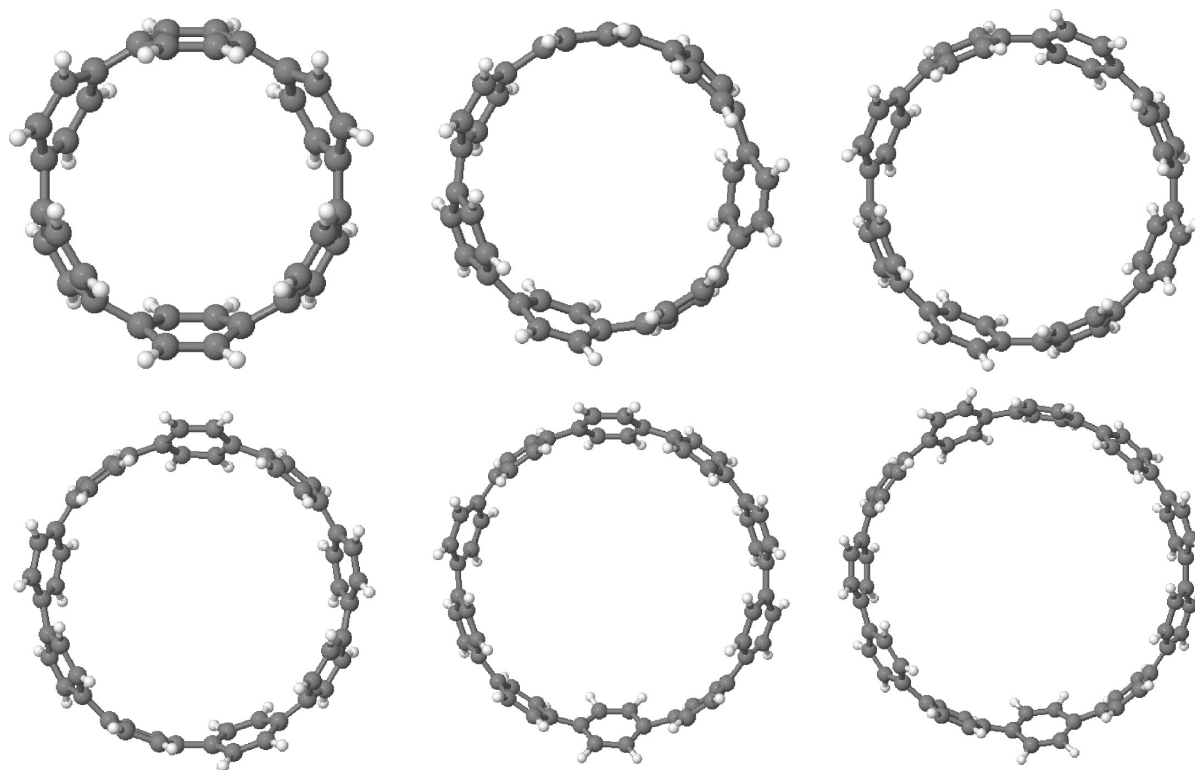
FIGURE 1. The neutral [*n*]CPs, *n* = 6−11. Please note that the molecules have different diameters but they are plotted with the same size and hence the atom balls appear larger for [6]CP and smaller for [11]CP. The figure is plotted with JMOL.[33]

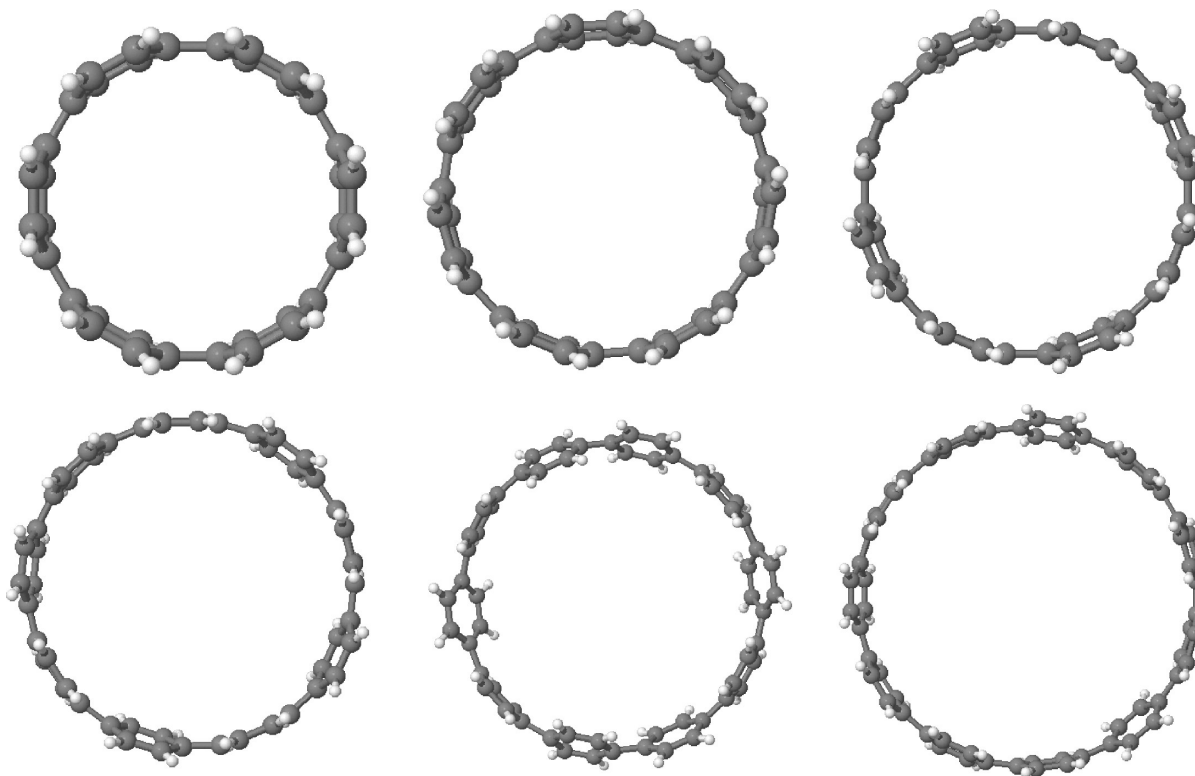**FIGURE 2.** The dianionic [*n*]CPs, *n* = 6−11. Please note that the molecules have different diameters but they are plotted with the same size and hence the atom balls appear larger for [6]CP^{2-} and smaller for [11]CP^{2-}. The figure is plotted with JMOL.[33]

point groups are the following: [6]CP, D_{3d}; [7]CP, C_2; [8]CP, D_{4d}; [9]CP, C_2; [10]CP, C_s; and [11]CP, C_1.

The nonplanarity of the phenylene rings is also decreased as the nanohoop diameter increases. In [6]CP, the rings are

bent by 16°, while the corresponding torsional angle in the [9]CP is 8°. The [7]CP and [8]CP lie in between. In [10]CP and [11]CP, the torsional angles vary among the phenylene rings and are roughly 7−11°.

The staggering angle, or the torsional angle between two adjacent phenylene rings, varies as well. In [6]CP and [8]CP it is 29−30°, while the low-symmetry nanohoops display a larger range of torsional angles between 13° and 40°. The irregularity in the structure of [10]CP and [11]CP agrees with the findings by Segawa et al., who observed a high flexibility of the larger nanohoops and suggested that in [12]CP the benzene rings would be able to rotate rather freely at room temperature.[19]

2.1.2. The Dianions $[n]CP^{2-}$. The dianionic nanohoops are shown in Figure 2. All the dianions have a singlet ground state. The dianions, $[6]CP^{2-}$ and $[7]CP^{2-}$, possesses a D_{6h} and D_{7h} symmetry, respectively. The phenylene rings are planar and perpendicular with respect to the nanohoop plane, i.e., they are not tilted as in the neutral counterparts. The torsional angle between the phenylene rings is practically zero. The phenylene rings display a larger bond length alternation than in the neutral nanohoops, with bond lengths of 143 and 138 pm in $[6]CP^{2-}$. In $[7]CP^{2-}$, the corresponding bonds are 2 pm shorter. The shortest bonds are the ones at the edges. The bond length of the bridging C−C bond is 145 pm in both dianions, or 3 pm shorter than in the neutral nanohoops. The dianionic $[n]$CPs thus have a quinoid structure, indicating a promoted electron delocalization along the cycloparaphenylene ring. The dianions are structurally very similar to the nanohoops in their first excited state.[21]

The dianions with eight and nine phenylene rings display the same structural features as the smaller dianionic $[n]$CPs. The point group symmetries of $[8]CP^{2-}$ and $[9]CP^{2-}$ are D_{4d} and C_2, respectively, showing that these larger nanohoops are not completely symmetrical, but adjacent benzene rings are slightly staggered with torsional angles of about 9°. The bridging C−C bond lengths of $[8]CP^{2-}$ are 145 pm, while the phenylene bonds are 138 and 142 pm. In $[9]CP^{2-}$, the corresponding bond lengths are 148, 139, and 141 pm.

The structure of the dianion $[10]CP^{2-}$ is similar to that of the neutral counterpart [10]CP. The C−C bond lengths of the phenylene rings are 138−139 and 140 pm while the bridging bonds are 148 pm. The corresponding bond lengths in $[11]CP^{2-}$ are 138, 141−142, and 146 pm. Adding two electrons does not result in a higher geometrical symmetry of the largest nanohoops, but in $[11]CP^{2-}$ the shortened bridging bond does indicate a larger electron delocalization as compared to the neutral [11]CP.

Computationally it has to be kept in mind that the dianions should be stabilized by counterions in order to render all orbital energies negative. The fact that the highest orbital energies of the dianions are positive at the DFT level should, however, not be a problem for the structural and magnetic properties. The lack of counterions also enables separation of the stabilization by the addition of two electrons and the possible further stabilization by the bonding between the positive counterions and the dianionic nanohoop.

The frontier orbitals of [6]CP shown in Figure 3 give qualitative support to the above arguments that the dianions have
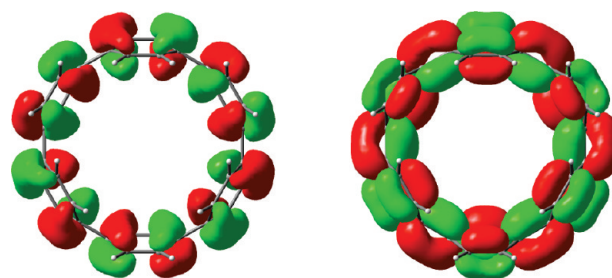
(33) JMOL: an open-source Java viewer for chemical structures in 3D; http://www.jmol.org.

FIGURE 3. The frontier orbitals of the neutral [6]CP. The highest occupied molecular orbital (HOMO; left) is more localized than the lowest unoccupied molecular orbital (LUMO; right), suggesting that the π-orbitals of the dianions are delocalized.
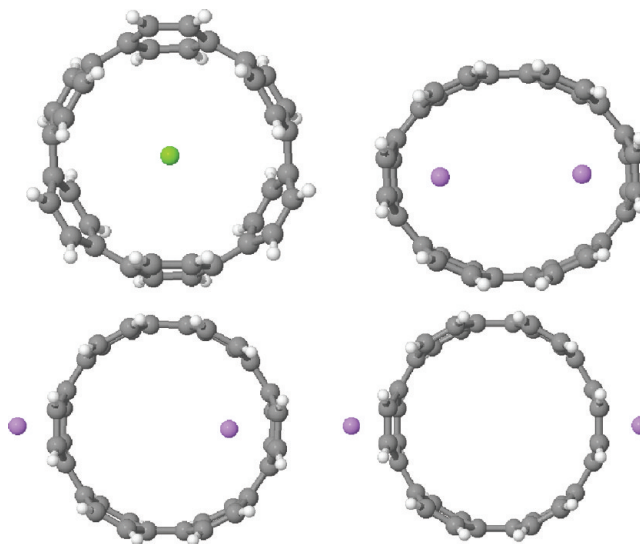

FIGURE 4. The magnesium and the dilithium complexes of [6]CP: Mg[6]CP and Li₂[6]CP in the upper row and Li₂[6]CP′ and Li₂-[6]CP″ in the lower row. The figure is plotted with JMOL.[33]

a stronger electron delocalization than the neutral nanohoops. The lowest unoccupied molecular orbital (LUMO) has a delocalized π character, whereas the highest occupied molecular orbital (HOMO) appears localized to the arene rings.

2.1.3. Li₂[6]CP and Mg[6]CP. Two metal complexes of [6]CP were optimized to further probe the ring current effects in the dianion. Mg[6]CP and the three investigated isomers of Li₂[6]CP are shown in Figure 4. Li₂[6]CP is formally a dianion of [6]CP hosting two Li⁺ cations. The complex is elliptic with a D_{2h} symmetry. The Li⁺ ions are situated 159 pm from the center of the closest phenylene ring, while the Li···Li distance is 534 pm. The bond lengths between the carbon atoms in the nanohoop agree with the bond lengths of the empty [6]CP dianion within less than 1 pm. The diameter of the single dianion is 833 pm, while the ellipsoidal lithium complex has the conjugate and transverse diameters of 756 and 905 pm, respectively. The Li atoms can also bind to the nanohoop from outside. Two hypothetical complexes were optimized to probe the effect of changing the binding site of the metals: In Li₂[6]CP′, the two lithium atoms are on the outside of the nanohoop, at the same six-membered rings as in the main complex Li₂[6]CP, while in Li₂[6]CP″, the other Li atom is situated on the outside and the other on the inside
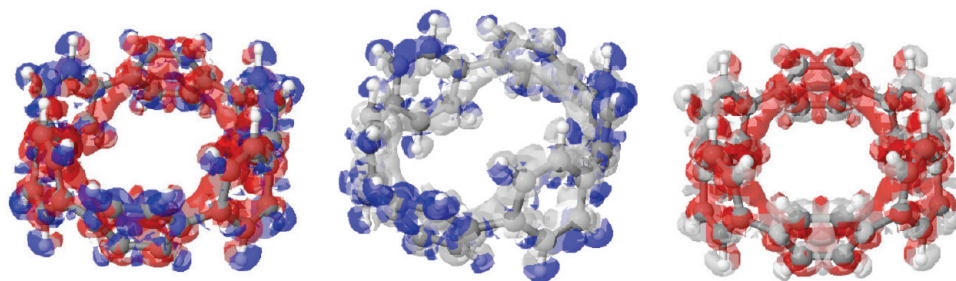
FIGURE 5. The current density distribution in [6]CP. Left: The diamagnetic component is plotted in blue and the paramagnetic component is red. Middle: The diamagnetic component follows the outer edges of the phenylene rings. Right: The paramagnetic component follows the edges tilted inward. The figure is plotted with JMOL.[33]

TABLE 1.   The Magnetically Induced Currents (in nA/T) in the [*n*]CPs[a]

molecule		six-membered ring		bridge
[6]CP		0.0	−5.5	−3.8
[7]CP		2.0	4.1	3.2
[8]CP		3.0	2.4	0.2
[9]CP		3.0	2.4	0.6
[10]CP		2.6	4.3	−0.4
[11]CP		5.0	3.9	1.0
[6]CP^{2-}		14.3	14.2	28.5
[6]CP^{2-}	SCF	18.3	18.2	35.7
[6]CP^{2-}	MP2	16.6	16.6	32.3
[7]CP^{2-}		15.3	15.6	31.5
[7]CP^{2-}	SCF	20.2	20.2	39.9
[7]CP^{2-}	MP2	17.8	17.8	34.8
[8]CP^{2-}		16.9	17.7	35.0
[8]CP^{2-}	SCF	20.6	20.6	41.6
[8]CP^{2-}	MP2	20.4	21.4	41.5
[9]CP^{2-}		18.1	16.8	35.3
[10]CP^{2-}		14.6	8.1	24.1
[11]CP^{2-}		16.6	18.7	34.7
Li$_2$[6]CP		11.0	11.0	26.9
Li$_2$[6]CP′		13.8	13.8	27.5
Li$_2$[6]CP″		13.8	13.8	27.5

[a]The dianions are indicated by the superscript "2−". The currents passing the two edges of the phenylene rings are listed in the middle columns. All the current strengths are calculated at the BP86/def2-TZVP level except for those marked with "MP2" or "SCF", which are obtained at the MP2/def2-SVP and at the SCF/def2-SVP levels, respectively.

FIGURE 6. The current density distribution in [7]CP. The diamagnetic component is plotted in blue and the paramagnetic component is red. Left: The neutral [7]CP. Right: The dianionic [7]CP^{2-}. The figure is plotted with JMOL.[33]

of the nanohoop. The Li$_2$[6]CP′ complex has a practically circular nanohoop and the symmetry is D_{2h} while Li$_2$[6]CP″ is slightly more elliptic with a C_{2v} symmetry. The bond lengths of the arene rings are 137−138 and 141−142 pm, while the bridging bonds are 144−145 pm. These complexes appear more loosely bound than Li$_2$[6]CP as the distance of the outer Li ions to the closest arene ring center is 192 pm as compared to 159 pm for the Li ion on the inside.

We also attempted to complexate magnesium with [6]CP in order to investigate whether a divalent single atom can stabilize the nanohoops in a similar way as the two monovalent lithium atoms do. A stationary point was found on the potential energy surface when the magnesium atom is at the center of the nanohoop. This is, however, a saddle point as indicated by one imaginary frequency. The normal mode corresponding to this frequency corresponds to the magnesium atom vibrating perpendicularly to the nanohoop plane. Natural population analysis and inspection of the molecular orbitals show no overlap between the Mg and the carbon atoms, and no electron transfer from the magnesium atom to the nanohoop. The bond lengths of the nanohoop in the Mg[6]CP complex are as in the neutral
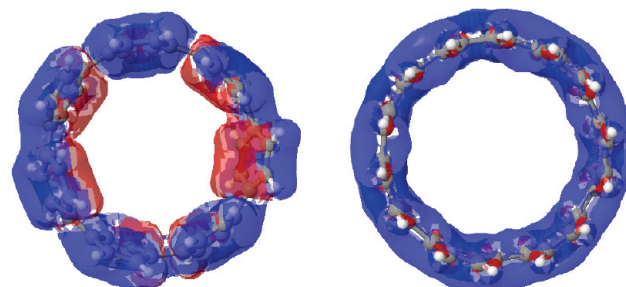
[6]CP, apart from the bridging C−C bonds being slightly elongated to 149 pm.

2.2. Magnetically Induced Currents. 2.2.1. The Neutral [*n*]CPs. The ring currents of the nanohoops are listed in Table 1. In [6]CP, a delocalized current of almost −4 nA/T circles around the nanohoop. In comparison, the ring current in benzene is 11.5 nA/T at the same BP86/def2-TZVP computational level. Thus, [6]CP is slightly antiaromatic by the ring current criterion. Figure 5 shows the diamagnetic and paramagnetic current densities in [6]CP. The paramagnetic component of the current follows the edge of the phenylene rings that is tilted toward the center of the nanohoop, while the majority of the diamagnetic component follows the edges that are tilted outward. The paramagnetic current path around the nanohoop follows a 24 π electron route, which by the Hückel $4n + 2$ rule for aromaticity corresponds to antiaromatic or nonaromatic character. The phenylene rings of [6]CP are nonaromatic and sustain no net current, but they function as junctions splitting the current.

The [7]CP sustains a net diatropic current of about 3 nA/T. This correlates with its 42 π electrons that imply a possible aromaticity. Figure 6 shows that the current density distribution of [7]CP is different from that of [6]CP. In [7]CP, there are three local biphenylene-like moieties while the benzene ring on the C_2 axis has a slightly more localized ring current.

The net ring currents distributed along all the nanohoops with 8−11 phenylene rings are composed of positive and negative components of equal absolute magnitude. The net ring current is thus zero and the nanohoops can be considered as nonaromatic. The very small net current in [11]CP may partly be due to leakage from adjacent arenes since the nanohoop structure is quite puckered. The calculated current
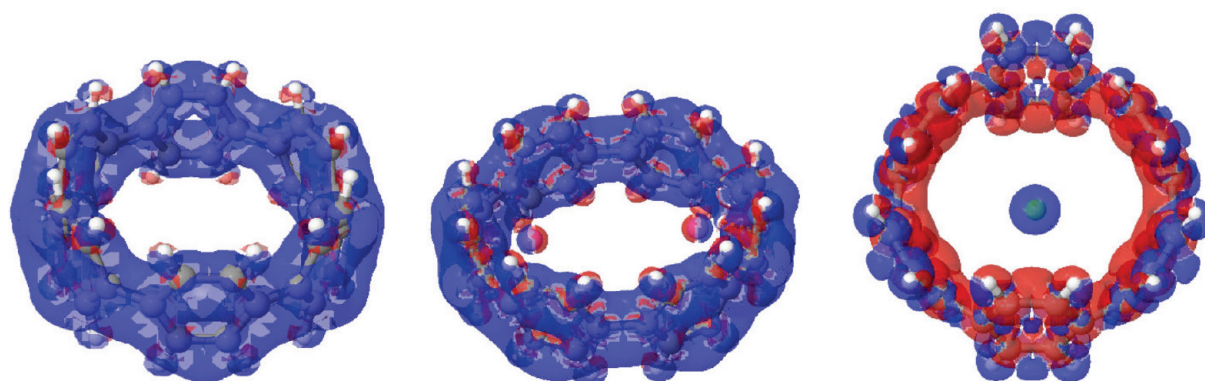
FIGURE 7. The current density distribution in the dianion (left), the dilithium complex (middle), and the magnesium complex (right) of [6]CP. The diamagnetic component is plotted in blue and the paramagnetic component is red. The figure is plotted with JMOL.[33]

can also be expected to be somewhat divergent because gauge invariance and charge conservation are obtained only in the limit of complete basis sets.[24,34]

There is a positive net current of the magnitude 2−5 nA/T in the phenylene rings of the nanohoops with $n = 7$−11. The phenylene rings are most planar in [11]CP, which can explain the improved electron delocalization in the phenylene moieties of the larger rings. Previously it was shown that benzene rings fused to antiaromatic molecules sustain a net current while the benzene rings fused to overall aromatic molecules only split the current which is delocalized over the whole molecule.[6]

2.2.2. The Dianions $[n]CP^{2-}$. The ring current in the dianion $[6]CP^{2-}$ is strongly diatropic with a net current of 28.5 nA/T. At the MP2/def2-SVP level, the current strength is somewhat larger at 32.3 nA/T while 35.7 nA/T is obtained at the SCF level. This corresponds very well with the Hückel aromaticity of this 38 π electron molecule. The current criterion for aromaticity correlates well with the observed bond length equalization of the bridging C=C bonds with respect to the conjugated bonds in the phenylene rings. At the same time, however, the bond lengths of the phenylene rings have become more alternated with respect to the neutral [6]CP and it is shown that no definitive quantitative conclusions upon the ring currents should be made solely on the basis of bond length alternations.

The dianion $[7]CP^{2-}$ has 72 π electrons, which is expected to correspond to anti- or nonaromaticity. The reduced bond length alternation with respect to the neutral [7]CP points to electron delocalization. The induced ring current susceptibility strength of 32 nA/T at the DFT level and 34.8 nA/T at the MP2 level is, however, strongly diatropic. At the SCF level, the current susceptibility strength is 39.9 nA/T. Thus, the ring current seems to agree with the geometrical characteristics upon the aromaticity of this 4n π electron system apparently violating the Hückel rule. Adding 2 phenylene rings or 12 π electrons yielding $[9]CP^{2-}$ will maintain the 4n electron count, but still the current susceptibility of 35 nA/T is diatropic.

There is strong diatropic current flowing along $[8]CP^{2-}$. The current susceptibility strength is 35 nA/T or about 6.5 nA/T stronger than in [6]CP. At the MP2 level the current strength is 41.5 nA/T and at the SCF level it is 41.6 nA/T.

Somewhat surprisingly, also $[10]CP^{2-}$ sustains delocalized diatropic current although structurally a benzenoid character would have been expected. The net current of 24 nA/T is not divided equally along the branches at each phenylene ring, but a somewhat larger component flows along the outer edge. The other dianionic nanohoops with eight or more phenylene rings have a current susceptibility strength of about 35 nA/T and possess a similar structural stabilization, while $[10]CP^{2-}$ forms an exception regarding both the structure and the ring current. The largest dianionic nanohoop $[11]CP^{2-}$ does display a slightly smaller bond length alternation and smaller staggering angles between the phenylene rings as compared to the neutral [11]CP, and consequently the ring current is equally divided along the edges of the phenylene rings.

The odd-n dianions seem to violate the Hückel (4n + 2) rule, since they all have a total of 4n π electrons. This can be explained in a hand-waving fashion by considering the electron delocalization paths along the nanorings as following either of the phenylene ring edges. Then every nanohoop would have two superimposed ring current delocalization pathways with 4n electrons each. Adding two electrons will thus give (4n + 2) π-electron systems.

In practice, small aromatic dianions have very short lifetimes.[35] The instability of polycyclic dianions can be overcome by introducing positively charged counterions such as lithium or sodium.[36] The effect of the counterions on the ring currents of the nanohoops is discussed below.

2.2.3. Li$_2$[6]CP and Mg[6]CP. The complex Li$_2$[6]CP has a similar bond length alternation and symmetrical structure with the phenylene rings perpendicular to the nanohoop plane, as the dianion of [6]CP. The aromatic character can thus be expected to be similar, although hasty conclusions about the ring currents should be avoided. The current density in the lithium complexed nanohoop is dominated by a strong diamagnetic component, yielding a net current of 28 nA/T. The arene rings split the current pathway equally, as expected from their symmetrical alignment along the nanohoop. The similarity in the current density distributions of the dianion $[6]CP^{2-}$ and the Li$_2$[6]CP complex is striking, as seen in Figure 7. The Li$_2$[6]CP′ and Li$_2$[6]CP″ complexes with either or both of the lithium ions outside the nanohoop

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sustain ring currents of the same strength as the internal complex Li$_2$[6]CP. This further supports the view that the lithiums only function as counterions stabilizing the dianionic nanohoop but they do not affect the magnetically induced currents.

Whereas the dilithium complex of [6]CP resembles the dianion, the magnesium complex Mg[6]CP features the same topology of the molecular structure and the current distribution as the corresponding neutral nanohoop. The current susceptibility strengths are also the same in Mg[6]CP and in neutral [6]CP. Since Mg[6]CP represents a saddle point, we do not consider it further here.

2.3. The ^{1}H NMR Chemical Shieldings and Nucleus-Independent Chemical Shifts. The ^{1}H NMR chemical shieldings of one certain proton in hydrocarbon nanorings are very sensitive to the global ring current.[6] In the nanohoops, the ^{1}H chemical shieldings show a correlation with the global ring current, although the picture here is not very straightforward. In the dianion and the dilithium complex, the ^{1}H chemical shieldings are indeed typically "aromatic". In the dianion [6]CP^{2-}, the proton shieldings are 27.8 and 28.0 ppm while in the Li2[6]CP they are between 26.8 and 27.7 ppm. The ^{1}H NMR chemical shielding for benzene is 24.3 ppm at the same computational level. In the slightly paramagnetic and nonaromatic nanohoops, i.e., the neutral [n]CPs, the ^{1}H NMR chemical shieldings are distributed between 23.4 and 24.1 ppm. The [6]CP does not stand out with respect to the other neutral nanohoops, although it sustains a stronger paramagnetic current. In the larger dianions the ^{1}H NMR chemical shieldings are between 24 and 30 ppm, the range being larger in the largest dianionic nanohoops. This indicates that the ring current is not the only aspect affecting the NMR chemical shieldings of the protons in multiring molecules, although it is a major effect when the current is strong. It is not straightforward to deduce the strength of the paratropic or diatropic currents in these molecules only from the proton NMR chemical shieldings.

The nucleus-independent chemical shifts were calculated at the center of the nanohoop, denoted as NICS(c) below, as well as at the center of one of the phenylene rings. At the phenylene rings, the NICS(0) was computed in the ring plane, NICS(1) was computed at 1.0 Å perpendicular distance from the ring outside the nanohoop and NICS(−1) was similarly computed 1.0 Å inside the nanohoop. For the neutral nanohoops the NICS(c) values are between −2.5 and −1.1 ppm, being largest for [6]CP and decreasing with the diameter of the nanohoop. At the phenylene ring of the neutral nanohoops, NICS(0) is between −6 and −7 ppm. NICS(1) and NICS(−1) are roughly of the same magnitude and range between −7 and −14 ppm, being more negative for the larger nanohoops. The paratropic character of [6]CP is not described by any of the NICS indices, since a positive NICS value would be expected for antiaromatic systems.

For the dianions, the NICS(c) values are strongly negative, reflecting the pronounced diatropic character. The NICS(c) values range from −15 to −8 ppm, generally decreasing with increasing diameter, as also observed for the neutral nanohoops. The decrease of the NICS(c) values can be explained by the increasing distance from the probe at the center of the nanohoop to the current path. A similar trend has also been observed previously for antiaromatic molecules.[29] The NICS(−1) values for the phenylene rings of the dianions

TABLE 2. Current Strengths (J in nA/T), ^{1}H NMR Shielding Ranges (σ in ppm), and NICS Values (in ppm)[a]

molecule	J	$\sigma(^1H)$	NICS(0)	NICS(1)	NICS(−1)	NICS(c)
[6]CP	−3.8	23.7	−6.9	−8.6	−8.9	−2.1
[7]CP	3.2	23.3−23.9	−5.8	−7.2	−8.1	−1.9
[8]CP	0.2	23.6−24.1	−7.0	−9.5	−10.1	−2.0
[9]CP	0.6	23.5−24.2	−6.3	−7.6	−9.0	−1.6
[10]CP	−0.4	23.6−24.1	−6.8	−9.2	−10.4	−1.4
[11]CP	1.0	23.4−24.1	−0.0	−14.0	−13.4	−1.1
[6]CP^{2-}	28.5	25.8−28.0	−10.4	−4.4	−21.6	−16.2
[7]CP^{2-}	31.5	27.6−28.2	−9.4	−3.9	−22.3	−15.1
[8]CP^{2-}	35.0	27.2−29.6	−9.1	−3.8	−22.2	−13.6
[9]CP^{2-}	35.3	26.5−30.1	−8.4	−3.4	−21.7	−12.2
[10]CP^{2-}	24.1	23.2−29.8	−6.1	−7.2	−17.1	−7.8
[11]CP^{2-}	34.7	25.1−29.7	−7.8	−4.1	−20.8	−10.0

[a]Current strengths and ^{1}H NMR shieldings are calculated at the BP86/def2-TZVP level while NICS values are obtained at the BP86/def2-SVP level. The current strength is computed across the bridging bonds between arene rings. NICS(0) is computed at the center of a benzene ring, NICS(1) at a position 1 Å perpendicularly outside the benzene ring, and NICS(−1) 1 Å from the benzene ring on the inside of the nanohoop. NICS(c) is computed at the center of the nanohoop.

correlate most clearly with the calculated ring current strengths although the correlation is not completely quantitative. NICS(1), and NICS(0) show rather an inverse correlation with the current strength. The deviation of [10]CP^{2-} from the general ring current trend is qualitatively also captured by the NICS values, except for NICS(0), which shows somewhat more arbitrariness.

3. Conclusions

The magnetically induced currents in the [n]cycloparaphenylenes with $n = 6-11$ phenylene moieties, as well as in the dianion and the magnesium and dilithium complexes of [6]CP, were computed with the aid of DFT at the BP86/def2-TZVP level (Table 2). The induced current strengths and the current density distributions were determined and the aromatic character of the studied compounds was discussed based on these. The bond length alternation and the ^{1}H NMR chemical shieldings were furthermore related to the aromatic or antiaromatic character of the molecules.

Although the phenylene moieties in the neutral [n]CPs have equalized bond lengths, the [8]CP−[11]CPs are found to be nonaromatic with zero net ring currents. [6]CP with $4n$ π electrons is slightly antiaromatic with a ring current of −4 nA/T, whereas [7]CP with $(4n+2)$ π electrons along the conjugation path is slightly aromatic with a current strength that is about 30% of the ring current strength in benzene. Thus, the ring current picture stands in contrast with earlier results indicating that [6]CP has a benzoid character.[23] The phenylene rings of the [n]CPs with eight or more phenylene rings sustain local ring currents of 2−5 nA/T. This correlates well with the observation that the excitation energies of the larger [n]CPs are independent of the ring size. This phenomenon was ascribed to localization of the excitons to the phenylene rings.[20,21]

The dianion [6]CP^{2-} and the dilithium complex formally described as [Li$_2$]$^{2+}$[[6]CP]$^{2-}$ sustain a strong diatropic current of 28.5 nA/T and are aromatic. The divalent magnesium atom does not stabilize the [6]CP molecule in the same way as two monovalent lithium atoms, and the Mg[6]CP complex appears unbound.

All the dianions of the investigated nanohoops with up to 9 arene rings possess a higher structural symmetry than the corresponding neutral molecules. The increased current delocalization correlates with structural stabilization, as is indicative for an aromatic system. This stabilization resembles the one typical for endohedral metallofullerenes and might be utilized in the design of novel supramolecular complexes. The current strengths are 10−18% stronger at the MP2 level as compared to DFT, while SCF yields 0−15% stronger currents than MP2.

The ^{1}H NMR chemical shieldings and the nucleus-independent chemical shifts of the nanohoops qualitatively reflect their aromatic character. The NICS values do not correlate quantitatively with the magnetically induced ring current susceptibilities. The bond length alternation between the conjugated bonds in the phenylene rings and the bridging C−C bonds between the rings is indicative for the electron delocalization along the nanohoop. The quinoidic character of the dianions correlates with a delocalized current density distribution. In the neutral [*n*]CPs, the arene rings have benzenoid character and only a weak or no net current density is distributed along the nanohoop. In some cases a significant ring current can be observed although the stabilization is not seen in the structure, as demonstrated by the dianion [10]CP^{2-}.

There is no clear odd−even trend in the aromaticity of the [*n*]CPs, with regard to the amount of phenylene rings, as judged by ring currents, ^{1}H NMR chemical shieldings, and bond length alternations. There is a clear connection between highly symmetrical quinoidic structures, increased electron delocalization, and the strength of the induced current susceptibility.

4. Computational Methods

The molecular structures of the [*n*]CPs were preoptimized at the density functional theory level with Becke's three-parameter functional[37] with the Lee−Yang−Parr correlation functional[38] (B3LYP) in combination with the 6-31G(d,p) basis set. Frequency calculations were performed for the optimized geometries to check whether they correspond to energy minima on the potential energy surface. The calculations were performed with Gaussian 03.[39] The molecular structures were further optimized with the BP86 functional[40,41] utilizing triple-ζ quality basis sets augmented with polarization functions (def2-TZVP).[42] The nuclear magnetic shieldings were calculated at the same level of theory. The nucleus-independent chemical shifts (NICS)[43] were calculated at the BP86/def2-SVP level.[42] The latter geometry optimizations and shielding calculations were performed with TURBOMOLE.[44] The current densities were obtained with GIMIC, which is an independent program using the perturbed and unperturbed density matrices from the nuclear magnetic shielding calculations.[24] The GIMIC program is freely available on request from the authors. Since DFT is known to in some cases overestimate delocalization effects in conjugated systems,[45] the NMR chemical shieldings and the magnetically induced current densities were also calculated at the SCF and MP2 levels by using the def2-SVP basis set for the dianionic [*n*]CPs with 6, 7, and 8 phenylene rings.

In the GIMIC method, the strength of the magnetically induced current susceptibility circling around the molecules is obtained by numerical integration of the current density. In the calculations, the magnetic field is directed along the *z*-axis directed perpendicularly to the [*n*]cycloparaphenylene ring.

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