

Aromaticity Induced by Electric Field: The Case of Polycalicenes

Justyna Dominikowska,^{*,†} Tadeusz Marek Krygowski,[‡] Wojciech Piotr Ozimiński,[§] and Marcin Palusiak[†]

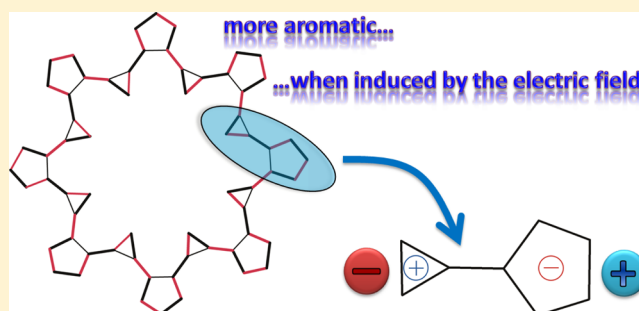
[†]Department of Theoretical and Structural Chemistry, Faculty of Chemistry, University of Łódź, Pomorska 163/165, 90-236 Łódź, Poland

[‡]Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

[§]National Medicines Institute, Laboratory of Theoretical Methods and Computation, Chełmska 30/34, 00-725 Warsaw, Poland

Supporting Information

ABSTRACT: Local and global π -electron delocalization occurring in planar poly-1,7-[*N*]calicenes is investigated with use of 10 aromaticity measures based on different physical properties. Systematic change of aromatic character is observed along chains of connected calicene units. Multidimensionality of the aromaticity phenomenon is studied with use of principal component analysis (PCA). The structural characteristics are compared with the properties of the isolated calicene molecule exposed to external electric fields of various intensities. Interrelations between the value of electric field applied and physical properties of the calicene molecule are discussed in the context of calicene unit affected by its surroundings in polycalicene chains. The patterns of global π -electron delocalization are described in graph theory terminology, and interconnections between local and global aromaticity in these systems are established.



INTRODUCTION

Calicene (triapentafulvalene, 5-(cycloprop-2-en-1-ylidene)-cyclopenta-1,3-diene) belongs to a greater group of nonalternant hydrocarbons, fulvalenes.^{1,2} Calicene is built up of three- and five-membered rings, which, following the Hückel $4n + 2$ rule,³ tend to contain two and six π -electrons, respectively. The rings are linked by a double CC bond that allows a charge transfer between these rings to take place,⁴ as documented by electric dipole moment $\mu = 4.66$ D.⁵ As a consequence, a weak aromatic π -electron delocalization is observed. Introduction of electron-withdrawing substituents in the five-membered ring increases the molecule bipolarity, for example, 2,3-dicyano-7,8-diphenylcalicene has a dipole moment of $\mu = 14.3$ D.⁶ Interestingly, calicene is considered to be an “aromatic chameleon”, a molecule that in its lowest excited triplet (fulvenes) or quintet (fulvalenes) state has its dipole moment reversed in comparison to its singlet ground state.^{7,8} This finding is strongly connected with the fact that in its lowest quintet excited state, the calicene molecule tends to gain some aromaticity⁷ (which can be explained with Baird’s rule⁹). Two units of calicene when fused form a stable molecule, that is, bicalicene,^{10,11} which, despite $4n$ π -electrons in its perimeter,¹² manifests aromaticity, though in a complex way; apart from two nonionic Kekulé structures, there is also an important contribution from a “tetraionic” structure with two positively charged three-membered rings and two other negatively charged five-membered rings.⁵ This complex manifestation of aromaticity has been shown with use of topological resonance energies^{13,14} and with ring current maps.⁵ Similar findings have

been demonstrated for the ground states of bicyclic tricalicene and tricyclic tetracalicene,¹⁵ for which several different electronically excited biradical structures participate.¹⁶ Recently, it has been shown that π -electron delocalization in bicalicene can be tuned both by the substitution of hydrogen atoms with electron withdrawing or electron donating groups and by application of external electric perturbation.¹⁷

A computational investigation of some polycalicenes as novel nonbenzenoid aromatic molecules has been carried out.¹⁸ They are built up by varying the number of calicene subunits and may possess various bonding motifs (e.g., head-to-tail or head-to-head). Planar and so-called “belted” polycalicenes have been considered, and some interesting electrical, magnetic, and optical properties of these kinds of systems have been presumed. Recently, so-called “band” polycalicenes have been studied as possible CO₂ hosts.¹⁹ Also some planar poly-2,7-[*N*]calicenes were studied with use of NICS^{20,21} and NMR chemical shifts.²¹

In the present study, a whole series of planar poly-1,7-[*N*]calicenes is investigated in order to reveal their structural properties. The systems chosen for the study were calicene (I) and poly-1,7-[*N*]calicenes II–VIII, where $N \in \{2, 3, \dots, 8\}$, shown in Figure 1.

The notation used in the paper is as follows: the systems are numbered with Roman numerals corresponding to the number of calicene units that form the system, Indo-Arabic numerals

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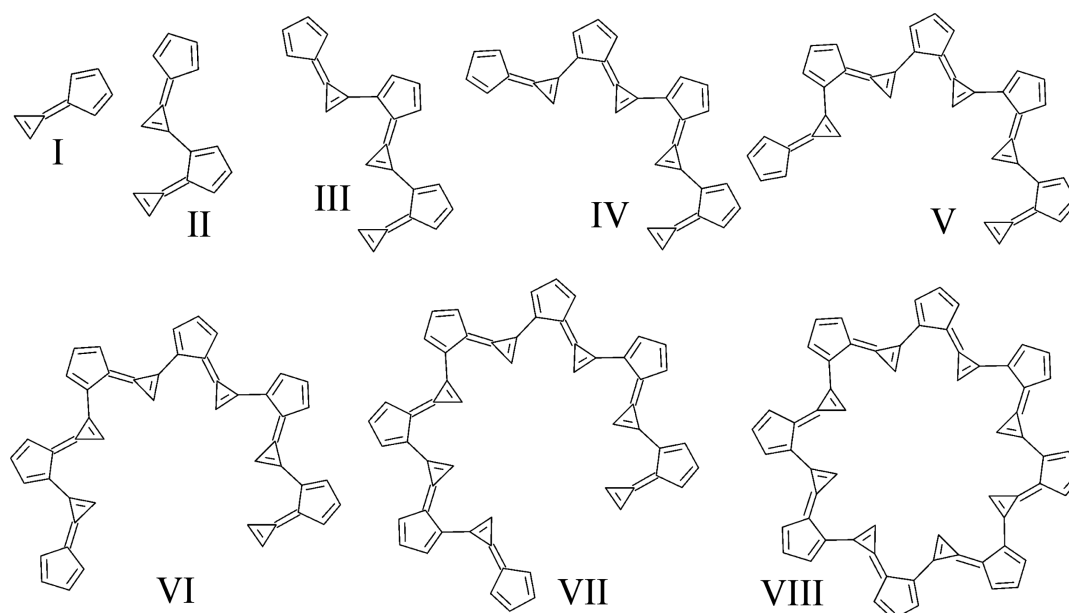


Figure 1. Systems I–VIII investigated in the study.

are used to number the calicene units in the polycalicyclic system. Three- and five-membered rings of the i th calicene unit are denoted as $T(i)$, and $F(i)$, respectively. For the bond linking $T(i)$ and $F(i)$, the $I(i)$ symbol is used. When the bond linking the i th and $(i+1)$ th calicene unit is considered, the symbol $L(i,i+1)$ is used. An example of the notation for system III is shown in Figure 2.

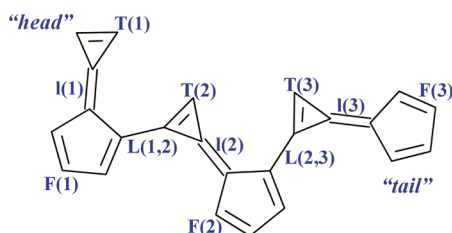


Figure 2. Example notation used in the study (for system III).

Please note that I and L denote, respectively, formally double and single bonds. Notation is simplified (T and F denoting three- and five-membered rings, respectively) in the case of system VIII (Figure 1), which possesses the D_{8h} symmetry.

The aim of the present study is to describe π -electron delocalization occurring in systems I–VIII and to reveal interconnections between local and global aromaticity. To fully understand the source of π -electron delocalization in polycalicycenes, the effect of external electric field exerted to calicene molecule is investigated. Rings being parts of systems chosen for the study also give a good opportunity to discuss the multidimensionality of aromaticity phenomenon.^{22,23} Full description of the methods and aromaticity measures used in the study are described in detail in Computational Methods Section.

RESULTS AND DISCUSSION

At the beginning, it is important to analyze the properties of bonds linking three- and five-membered rings. There are direct correlations between three structural parameters, namely, the bond length, two-center delocalization index,^{24,25} and bond

ellipticity²⁶ (absolute values of correlation coefficients $|R|$ are greater than 0.997). Thus, in further discussion, one of those parameters, namely, the bond length, is used. Taking into account that all of the systems I–VII possess an odd number of bonds, we might assign number 0 to the bond in the middle, and then assign consecutive integers to other ring-linking bonds (those that are closer to the three-membered molecule “head” have negative assignments and those that are closer to five-membered “tail”, the positive ones). In Figure 3, the linking-bond lengths for systems VI and VII are presented (according to the assignments made).

In Figure 3, it is clearly visible that the distinction between formally single bonds linking calicene units (L) and formally

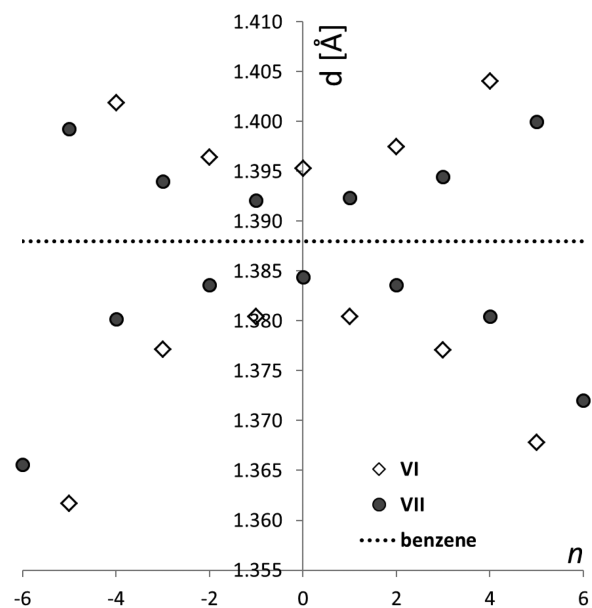


Figure 3. Scatter plot of linking bond lengths versus their position in systems VI and VII (0 is assigned to middle bond of each system, negative values denote bonds that are closer to the system “head” and positive ones, those closer to the system “tail”).

double bonds linking three- and five-membered rings in calicene unit (**1**) is physically meaningful, since their bond lengths are, respectively, longer and shorter than the bond lengths in benzene, an archetype for aromatic species. Another thing that should be pointed out is that the greater the number of calicene units in polycalicene, the closer the L and I bond lengths are to the CC bond length of benzene (see Figure 3, where only systems VI and VII are considered for clarity but the trend is exactly the same for each of the systems I–VIII). An important phenomenon takes place in the case of system VIII since the linking bonds lengths are 1.388 Å, which is exactly the same as in the benzene molecule, so that in this system I and L cannot be distinguished any more. One may notice that parts of a plot shown in Figure 3 are not symmetric in relation to the ordinate axis. Formally double bonds (**1**) are shorter when closer to the polycalicene “head” (n is negative) in comparison to the corresponding bonds close to the “tail” (positive n values), for example, VII-I(**1**) length is 1.366 Å, while VII-I(**7**), it is 1.372 Å. In the case of formally single bonds (L) linking calicene units, the bonds are longer when closer to the polycalicene “tail” (negative n values), for example, the VI-L(**1,2**) length is 1.402 Å, and for VI-L(**5,6**), it is 1.404 Å. However, the effect for L bonds is weaker than in the case of I bonds.

When local aromaticity of three- and five-membered rings is compared, HOMA,^{27,28} NICS,²⁹ and NICS(1)³⁰ indices show that the three-membered rings are more aromatic than the five-membered ones, for example, HOMA equals 0.40 for I-T(**1**) and nearly 0.25 for I-F(**1**). EL,³¹ FLU,³² and NICS(1)_{zz}³³ show the opposite trend. However, it is important to point out that some aromaticity indices are affected by the ring size (e.g., all types of NICS,^{34,35} HOMA was also suspected for ring size dependency, since its normalization constant is not adjusted when the number of atoms forming a ring is changed³⁶). Thus, it is necessary to consider aromaticity of the two groups of rings, three- and five-membered, separately, since in such a case a direct comparison is justified. Values of all aromaticity indices used in the study for three- and five-membered rings are presented in Tables S5 and S6 in Supporting Information, respectively.

HOMA values indicate nonaromatic or aromatic character of three-membered rings, depending on the number of calicene units in the molecule. π -Electron delocalization is the lowest in the case of T(**1**) rings for all the systems. For the three-membered rings, HOMA values are directly connected to the bond length alternation, since values of the EN³⁷ component of HOMA are very close to 0 and the slope coefficient of interrelation between HOMA and GEO³⁷ equals -1.001 . In the case of five-membered rings, EN values are more significant (of similar magnitude as GEO), but in the series of polycalicenes, HOMA mainly follows the GEO component, since EN values exhibit smaller changes (interval between 0.217 for VII-F(**7**) and 0.269 for II-F(**1**)) than GEO (interval between 0.121 for VIII-F and 0.498 for I-F(**1**)). There is a linear correlation between HOMA and FLU indications for both three- and five-membered rings (absolute values of correlation coefficients, $|R|$, are greater than 0.996). There is no interrelation between EL and HOMA (or FLU) for three-membered rings. Most probably this is because EL is based on bond ellipticities that are computed in bond critical points located on the bent bond paths (HOMA is based on bond lengths and FLU is based on delocalization indices, integrated over atomic basins). NICS does not correlate directly with any of the indices used in the

study, however, in the case of EL, NICS(1)_{zz} creates three groups of interrelations, namely, for T(**1**) rings, for T rings that are the closest to the polycalicene “tail”, and for the rest of T rings. A similar situation takes place when quantum theory of atoms in molecules (QTAIM)³⁸ parameters, electron density and total energy density (ρ_{RCP} and H_{RCP} , respectively), of the three-membered rings are compared with HOMA. Such series of interrelations are even more evident for the five-membered rings, for example, direct linear correlation between EL and HOMA can be noticed for F(**1**), “tail” F rings, while the more general trend can be found for the rest of five-membered rings (Figure 4).

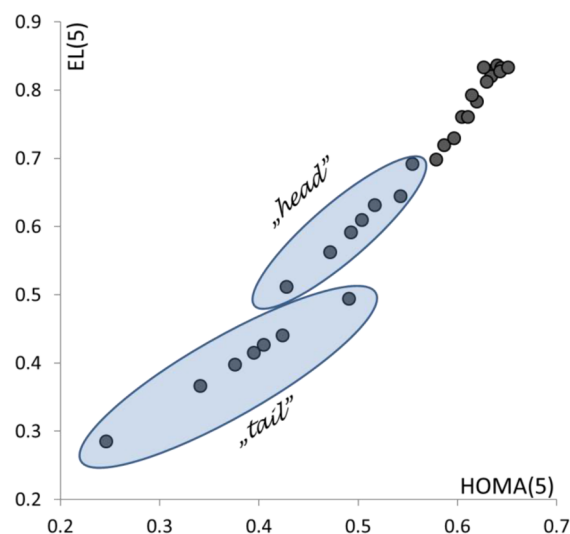


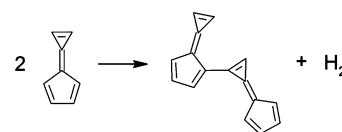
Figure 4. Dependence between EL and HOMA indices for five-membered rings.

The distinction between F(**1**), the “tail” F rings, and the rest of the rings appears also in dependences between all types of NICS, QTAIM parameters, and HOMA. This phenomenon can be explained if surroundings of “head”, “tail”, and the rest of the rings are considered.

Analyzing the values of various aromaticity measures collected in Tables S5 and S6 in the Supporting Information, one may consider the mean value of π -electron delocalization descriptors for systems I–VIII. Interestingly, the correlation (absolute values of correlation coefficients, $|R|$, are greater than 0.987) between mean values of aromaticity indices occurs, for indices directly using the reference value, namely HOMA, EL, and FLU (their mean values for systems are given in Table S7 in the Supporting Information). Mean values of aromaticity indices for systems II–VIII can be compared with energetic parameters of a hypothetical reaction of polycalicene formation from calicene units (example of the reaction for system II is shown in Scheme 1).

All values of energy parameters, namely, the reaction energy, zero-point corrected energy, enthalpy, and Gibbs free energy

Scheme 1



are given in Table S8 in the Supporting Information. Gibbs free energy values show unambiguously that polycalicyclic formation from calicene units is a spontaneous process. Interestingly, exponential relation between the mean value of HOMA index ($\text{HOMA}_{\text{mean}}$) and all of the energetic parameters of the reaction occurs (graphical representation of relation between $\text{HOMA}_{\text{mean}}$ and ΔG_r is shown in Figure 5).

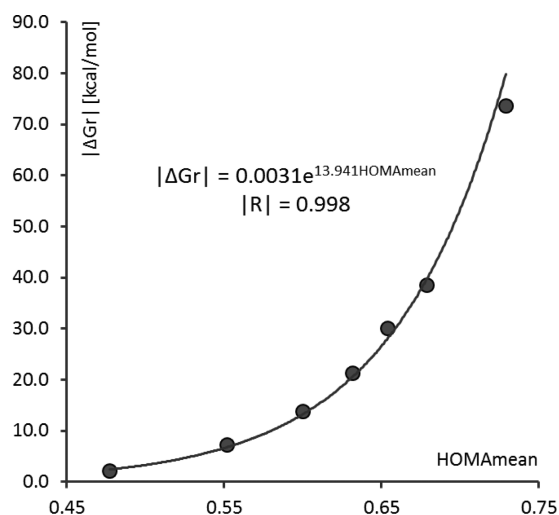


Figure 5. Relation between $\text{HOMA}_{\text{mean}}$ and ΔG_r (kcal/mol) for the reaction of polycalicyclic formation from calicene units.

This leads to a more general conclusion that for polycalicyclics aromaticity measures based on structural properties are directly related to energetic parameters of the hypothetical reaction of polycalicyclic formation from calicene units. The greater the aromatization in the system or, in other words, the greater the system, the more energetically favorable polycalicyclic formation is.

All aromaticity indices used in the study show rather weak aromatic character of the five-membered rings. HOMA and QTAIM based aromaticity indicators show that the “tail” five-membered rings are of lowest aromaticity in each system. NICS values rather do not depend on the unit position in the polycalicyclic, but the “tail” five-membered rings appear to be only slightly more aromatic according to the NICS indications. The observations made for the series of “head” and “tail” units can be confirmed with further statistical analysis. When considering the whole set of three- or five-membered rings

investigated in the study, the correlations between different aromaticity indicators are usually not satisfactory (see Tables 1 and 2 for correlation matrices of aromaticity estimators for all three- or five-membered rings, respectively). For 10 aromaticity measures described in the study, 45 correlation coefficients can be estimated. For a whole set of three-membered rings, there are 14 (~31%) correlation coefficients that satisfy a condition of $|R| \geq 0.9$ (values in bold in Table 1), and in the case of five-membered rings only 8 (~18%) correlation coefficients satisfy the above-mentioned condition (values in bold Table 2).

However, when taking into account the set of “head” three-membered rings, 25 (~56%) correlation coefficients are equal to or greater than 0.9 (Table 3, in bold). In the case of five-membered rings, when only “tail” units are considered, the condition $|R| \geq 0.9$ is satisfied by 34 (~75%) interrelations (see Table 4).

Thus, one may notice that the choice of rings of similar surroundings (in other words structurally similar) leads to much better correlations between various aromaticity measures. This conclusion is in line with a conclusion drawn in ref 23.

Hence systems investigated in the study contain three- and five-membered rings that are of great structural similarity, the data sets from Tables S5 and S6 may allow us to reveal the number of components of which the estimations of 10 aromaticity indices consist. Similar studies were performed earlier for different sets of systems,^{39,40} but those data sets could be affected by structural dissimilarities such as the ring size or the type of heteroatoms forming a ring. Principal component analysis (PCA)⁴¹ has thus been employed to reveal the most significant principal components corresponding to the aromaticity measures data obtained in the study and to verify the statement about the multidimensionality of aromaticity phenomenon.^{22,23} Please note that the composition of first principal components for each case of PCA is given in Tables S9–S12 in the Supporting Information. In the case of three-membered rings, two principal components (the first one 59%, the second 31%) are sufficient to explain 90% of data variance; the third one is needed for 99% data (gathered in Table S5) variance recovery. The PCA results for five-membered rings show two principal components that allow retrieval of 95% (the first one 71%, the second 24%) of data (Table S6) variance. When the third principal component is taken into account, 99% of data variance is explained. Hence, the principal component analysis for rings being parts of poly-1,7-[N]calicenes demonstrates that in that case aromaticity is at least a two-

Table 1. Correlation Matrix for the Aromaticity Measures Data Estimated for All Three-Membered Rings Investigated in the Study^a

	HOMA	EL	FLU	NICS	NICS(1)	NICS(1) _{zz}	ρ_{RCP}	H_{RCP}	G_{RCP}	V_{RCP}
HOMA	1.00									
EL	0.33	1.00								
FLU	-1.00	-0.30	1.00							
NICS	-0.98	-0.24	0.98	1.00						
NICS(1)	0.02	0.11	-0.06	-0.08	1.00					
NICS(1) _{zz}	0.26	0.13	-0.31	-0.30	0.95	1.00				
ρ_{RCP}	-0.33	-0.26	0.36	0.39	-0.93	-0.93	1.00			
H_{RCP}	0.42	0.29	-0.45	-0.47	0.89	0.92	-1.00	1.00		
G_{RCP}	0.18	-0.10	-0.15	-0.11	-0.95	-0.83	0.87	-0.82	1.00	
V_{RCP}	0.13	0.21	-0.16	-0.19	0.97	-0.91	-0.98	0.95	-0.95	1.00

^aThe values of $|R| \geq 0.9$ are in bold type.

Table 2. Correlation Matrix for the Aromaticity Measures Estimated for All Five-Membered Rings Investigated in the Study^a

	HOMA	EL	FLU	NICS	NICS(1)	NICS(1) _{zz}	ρ_{RCP}	H_{RCP}	G_{RCP}	V_{RCP}
HOMA	1.00									
EL	0.99	1.00								
FLU	-1.00	-0.98	1.00							
NICS	-0.49	-0.41	0.46	1.00						
NICS(1)	-0.92	-0.88	0.91	0.77	1.00					
NICS(1) _{zz}	-0.56	-0.49	0.54	0.99	0.83	1.00				
ρ_{RCP}	0.36	0.29	-0.32	-0.89	-0.61	-0.87	1.00			
H_{RCP}	-0.08	0.01	0.04	0.86	0.40	0.82	-0.92	1.00		
G_{RCP}	0.88	0.88	-0.85	-0.51	-0.84	-0.57	0.58	-0.24	1.00	
V_{RCP}	-0.82	-0.81	0.79	0.67	0.87	0.72	-0.75	0.46	-0.97	1.00

^aThe values of $|R| \geq 0.9$ are in bold type.

Table 3. Correlation Matrix for the Aromaticity Measures Data Estimated for “Head” Three-Membered Rings Investigated in the Study^a

	HOMA	EL	FLU	NICS	NICS(1)	NICS(1) _{zz}	ρ_{RCP}	H_{RCP}	G_{RCP}	V_{RCP}
HOMA	1.00									
EL	-0.51	1.00								
FLU	-0.99	0.39	1.00							
NICS	-0.91	0.78	0.85	1.00						
NICS(1)	-0.99	0.58	0.97	0.95	1.00					
NICS(1) _{zz}	-0.88	0.80	0.80	0.97	0.92	1.00				
ρ_{RCP}	0.99	-0.45	-1.00	-0.88	-0.98	-0.83	1.00			
H_{RCP}	-0.99	0.43	1.00	0.87	0.97	0.81	-1.00	1.00		
G_{RCP}	0.99	-0.44	-1.00	-0.87	-0.98	-0.83	1.00	-1.00	1.00	
V_{RCP}	-0.99	0.44	1.00	0.87	0.98	0.82	-1.00	1.00	-1.00	1.00

^aThe values of $|R| \geq 0.9$ are in bold type.

Table 4. Correlation Matrix for the Aromaticity Measures Data Estimated for “Tail” Five-Membered Rings Investigated in the Study^a

	HOMA	EL	FLU	NICS	NICS(1)	NICS(1) _{zz}	ρ_{RCP}	H_{RCP}	G_{RCP}	V_{RCP}
HOMA	1.00									
EL	1.00	1.00								
FLU	-0.99	-0.99	1.00							
NICS	-0.98	-0.99	0.99	1.00						
NICS(1)	-0.94	-0.94	0.96	0.96	1.00					
NICS(1) _{zz}	-0.96	-0.96	0.97	0.99	0.96	1.00				
ρ_{RCP}	0.98	0.98	-0.97	-0.93	-0.91	-0.89	1.00			
H_{RCP}	-0.96	-0.96	0.97	0.97	0.96	0.97	-0.93	1.00		
G_{RCP}	0.91	0.89	-0.88	-0.81	-0.79	-0.75	0.97	-0.82	1.00	
V_{RCP}	-0.97	-0.96	0.95	0.91	0.89	0.86	-1.00	0.92	-0.98	1.00

^aThe values of $|R| \geq 0.9$ are in bold type.

dimensional phenomenon.³⁹ In both cases, of three- and five-membered rings considered in the study, three principal components are needed for 99% aromaticity measures data recovery. To verify an assumption that the number of principal components of aromaticity relies on structural similarities between systems taken into account, principal component analysis was performed for two groups of “head” three- and “tail” five-membered rings. For the “head” three-membered rings, only two components are needed for 99% data variance recovery (the first one 89%, the second 10%). In the case of “tail” five-membered rings, only one component allows retrieval of 95% of data variance (the second component 4% leads to 99% data variance recovery). One may draw a conclusion that greater structural similarity leads to reduction of the number of components, since it was demonstrated that groups of “head” three- and “tail” five-membered rings demonstrate greater

structural similarity in comparison to the groups of all three- and five-membered rings present in polycalices.

Interestingly, the lateral (“head” and “tail”) rings are systematically less aromatic compared with the inner ones. Such situation should result from the fact that each calicene moiety is an electric dipole and as such it generates an external electric field, which influences neighboring individuals to some extent in an additive way. Hence, such field exerts its action most efficiently on the inner calicene moieties, and thus they are more polarized. Such polarization is connected with π -electron charge transfer (π -CT) between three- and five-membered rings leading to electronic structure of individual rings being closer to the $4n + 2$ magic number of π -electrons, and therefore, the inner rings become more aromatic than the lateral ones. In order to provide evidence for this assumption, we performed calculations in which the isolated calicene

molecule was exposed to the electric field acting along the molecular axis, as shown in Figure 6. The value of the field was between -0.025 and 0.025 au (positive values correspond to vector field directed as in Figure 6, while negative correspond to the opposite direction).



Figure 6. Orientation of calicene molecule in external electric field (\vec{F}).

Selected numerical values of quantities such as the electric field, dipole moment, total energy of the system, and HOMA for both rings are presented in Table 5 (all aromaticity measures values are given in Tables S13 and S14 in the Supporting Information).

Table 5. Parameters (HOMA for Three- and Five-Membered Rings, Total Energy and Dipole Moment) Of Calicene Molecule in the Presence of Electric Field \vec{F}

\vec{F} [au]	HOMA(3)	HOMA(5)	E [au]	μ [D]
-0.0250	0.787	0.631	-308.495	15.67
-0.0225	0.762	0.612	-308.480	14.51
-0.0200	0.733	0.588	-308.466	13.36
-0.0175	0.702	0.558	-308.454	12.23
-0.0150	0.669	0.524	-308.442	11.12
-0.0125	0.632	0.485	-308.432	10.01
-0.0100	0.591	0.442	-308.423	8.92
-0.0075	0.548	0.395	-308.414	7.84
-0.0050	0.502	0.345	-308.407	6.77
-0.0025	0.452	0.293	-308.401	5.71
0.0000	0.400	0.246	-308.396	4.66
0.0025	0.343	0.182	-308.392	3.61
0.0050	0.283	0.124	-308.389	2.56
0.0075	0.220	0.066	-308.387	1.52
0.0100	0.155	0.008	-308.386	0.47
0.0125	0.087	-0.050	-308.386	-0.58
0.0150	0.016	-0.107	-308.387	-1.64
0.0175	-0.056	-0.162	-308.389	-2.73
0.0200	-0.127	-0.214	-308.392	-3.86

It appears that, according to our expectations, when the field vector is directed as shown in Figure 6, the field amplifies the effect of intramolecular π -CT and the increase of aromaticity can be noticed. When the field vector is directed oppositely, the decrease of aromaticity is observed. These observations are in line with the results obtained for bicalicene by Mandado and Ramos-Berdullas.¹⁷ Changes in HOMA due to the change in field force are monotonic and can be expressed as a polynomial regression ($|R| = 0.999$, see Figure 7).

Changes in HOMA in both rings are intercorrelated linearly ($|R|$ for HOMA(3) vs HOMA(5) linear regression equals 0.998, graphically not shown here). The slope of linear regression between HOMA(3) and HOMA(5) equals 0.957, which shows that three-membered rings are slightly more susceptible to external electric field changes. It is also interesting that changes of the electric field imply changes in the total energy of the system, such that the maximum value (the least stable system) is for 0.01 au electric field value, exactly where HOMA(5) is

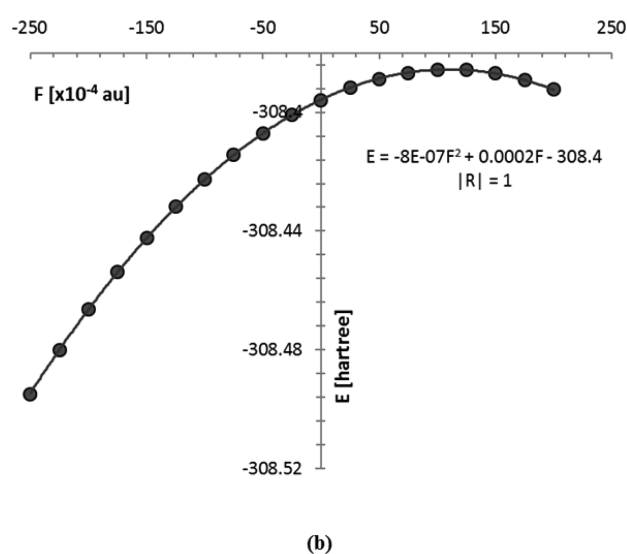
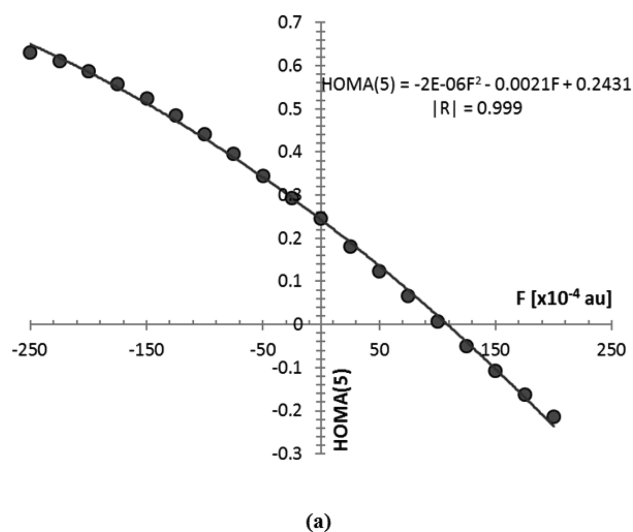


Figure 7. Dependences between HOMA index for five-membered rings (a) or system energy value (b), given in au, and the value of external electric field (au).

closest to zero, that is, where the π -CT shall also be closest to zero, as indicated by the smallest value of the dipole moment among the whole series (see Table 5). Therefore, one would postulate that the calicene system is of the lowest thermodynamic stability when the formal number of π -electrons in both rings is in the middle between $4n + 2$ and $4n$. When system goes to $4n + 2$ or $4n$, its thermodynamic stability rises. Unfortunately, further increase of the electric field cannot be exerted above 0.020 au due to wave function instability and problems in SCF convergence. Thus, the behavior of the calicene affected by the field of the values beyond the limits reached here remains unknown, at least for today.

Thus, the presence of more calicene units in the system can be compared with the presence of external electric field, when induction leads to greater aromaticity of three- and five-membered rings. Also, it is worth mentioning that changes in the aromaticity of individual rings are followed by changes in the length of the bond linking them. The bond becomes more of single character ($d_{cc} = 1.408$ Å for $\vec{F} = -0.025$ au) when

zwitterionic mesomeric form (right side in Figure 8) predominates.

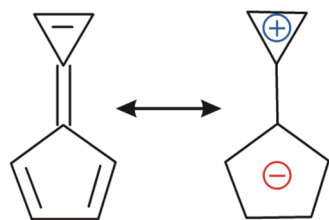


Figure 8. Mesomeric forms of calicene molecule without (left) and with (right) charge separation.

Considering the direct relationship between the value of electric field applied to calicene moiety and aromaticity of three- and five-membered rings, based on polynomial regression it is possible to estimate an approximate value of the electric field acting on the central calicene unit (due to the presence of neighboring units) in systems II–VIII, for example, π -electron delocalization in the five-membered rings of system VIII correspond to an electric field of ca -0.025 au.

To additionally support the conclusion on the role of the field effect, one may consider π -electron delocalization in the system shown in Figure 9 (distances between hydrogen atoms of the neighboring calicene units, 2.45 Å, are frozen, being slightly greater than the sum of van der Waals radii).

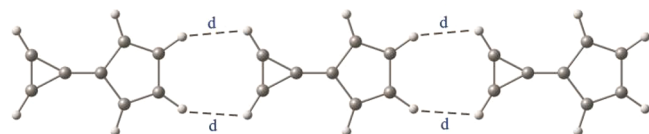


Figure 9. (Calicene)₃ system ($d = 2.45$ Å).

HOMA values for each of the rings in (calicene)₃ and for isolated calicene molecule are given in the Table 6.

Table 6. Values of HOMA Index for Calicene Molecule and for (Calicene)₃ System (CAM-B3LYP/6-311++G(d,p))

calicene unit	HOMA(3)	HOMA(5)
calicene (I)	0.400	0.268
calicene 1	0.432	0.297
calicene 2	0.435	0.310
calicene 3	0.411	0.282

It is important to note that in both cases, of three- and five-membered rings, π -electron delocalization is greater for each unit of (calicene)₃ than for the isolated calicene molecule. One may also notice that the internal calicene unit of (calicene)₃ has the highest HOMA values for both types of rings. The differences between values of HOMA index are very small in this case, but it can be explained with the fact that the distance between closest carbon atoms of adjacent calicene units amounts to 3.89 Å and the electric field force value diminishes by the square of the distance. These findings further support the conclusion concerning the induction role in aromatization of poly-1,7-[N]calicenes because π -electron conjugation is not present between calicene moieties in (calicene)₃ system.

When global π -electron delocalization is considered, there is a relationship between aromaticity of three- and five-membered

rings and HOMA and EL for I and L bonds. Since I and L bonds have different properties for systems I–VII, those two groups are treated separately (see Tables 7 and 8, respectively, for I and L bond length, HOMA, and EL values).

Table 7. Values of I Bond Parameters

system	ring no.	d_{CC} [Å]	HOMA(CC)	ϵ_{CC}	EL(CC)	$\delta(CC)$ [e]
I	I(1)	1.352	0.659	0.295	0.029	1.479
	II	I(1)	1.356	0.732	0.280	0.182
III	I(2)	1.362	0.821	0.267	0.310	1.432
	I(1)	1.358	0.769	0.273	0.256	1.435
	I(2)	1.369	0.905	0.243	0.558	1.385
IV	I(3)	1.364	0.854	0.261	0.370	1.419
	I(1)	1.359	0.789	0.269	0.294	1.428
	I(2)	1.373	0.940	0.231	0.672	1.365
V	I(3)	1.373	0.941	0.232	0.667	1.365
	I(4)	1.366	0.873	0.258	0.405	1.412
	I(1)	1.360	0.803	0.266	0.319	1.423
	I(2)	1.375	0.957	0.225	0.733	1.354
VI	I(3)	1.377	0.972	0.218	0.800	1.342
	I(4)	1.375	0.958	0.225	0.731	1.353
	I(5)	1.367	0.883	0.256	0.427	1.407
	I(1)	1.362	0.822	0.263	0.354	1.416
	I(2)	1.377	0.970	0.220	0.784	1.345
VII	I(3)	1.380	0.985	0.210	0.881	1.328
	I(4)	1.380	0.985	0.210	0.885	1.327
	I(5)	1.377	0.969	0.220	0.788	1.343
	I(6)	1.368	0.895	0.253	0.453	1.401
	I(1)	1.366	0.871	0.251	0.478	1.395
	I(2)	1.380	0.984	0.212	0.864	1.330
	I(3)	1.384	0.995	0.203	0.957	1.315
VIII	I(4)	1.384	0.997	0.200	0.984	1.310
	I(5)	1.384	0.995	0.202	0.967	1.313
	I(6)	1.380	0.985	0.211	0.880	1.328
	I(7)	1.372	0.935	0.242	0.559	1.379
	I(1)	1.388	1.000	0.189	0.905	1.292

Similarly to the dependences between aromaticity indices, there are separate dependences between ring and bond HOMA for “head”, “tail”, and the rest of the three- or five-membered rings (internal rings can be further divided into groups relying on the distance from “head” and “tail”, see Figure 10 for the example graphical representation of this phenomenon).

As was shown in the previous section, an obvious similarity between field effect and local π -electron delocalization in polycalicyenes exists. However, π -electron delocalization is somewhat different since in polycalicyenes pure inductive effect would lead to the zwitterionic structure with three- and five-membered rings linked with bonds of a single bond character. Instead of this effect in polycalicyenes, there are series of correlations between aromaticity of three- and five-membered rings and HOMA and EL of I and L bonds. Moreover the more calicene units the polycalicyene system consists of, the smaller difference between I and L bond lengths, and the bond lengths are more similar to the CC bond length in the benzene (fully aromatic system). These effects may be interpreted with use of graph theory.⁴² First let us consider the system VIII as a model. If we assume its resonance structure with no charge separation as an edge-weighted graph with carbon atoms as vertices and single and double bonds as weighted edges, we obtain the global π -electron delocalization pattern. When four different closed paths (of the same symmetry as its parent system) are

Table 8. Values of L Bond Parameters

system	ring no.	d_{CC} [Å]	HOMA(CC)	ϵ_{CC}	EL(CC)	$\delta(CC)$ [e]
II	L(1,2)	1.412	0.855	0.127	0.283	1.199
III	L(1,2)	1.407	0.902	0.138	0.388	1.214
	L(2,3)	1.409	0.890	0.137	0.379	1.212
IV	L(1,2)	1.405	0.926	0.144	0.453	1.223
	L(2,3)	1.402	0.946	0.151	0.526	1.233
V	L(3,4)	1.407	0.908	0.142	0.432	1.219
	L(1,2)	1.403	0.939	0.148	0.492	1.229
	L(2,3)	1.399	0.969	0.160	0.613	1.246
VI	L(3,4)	1.400	0.964	0.159	0.600	1.244
	L(4,5)	1.406	0.920	0.146	0.467	1.224
	L(1,2)	1.402	0.950	0.152	0.532	1.234
	L(2,3)	1.396	0.982	0.167	0.678	1.256
VII	L(3,4)	1.395	0.986	0.170	0.709	1.261
	L(4,5)	1.397	0.977	0.165	0.663	1.253
	L(5,6)	1.404	0.934	0.150	0.516	1.231
	L(1,2)	1.399	0.967	0.160	0.609	1.246
	L(2,3)	1.394	0.991	0.174	0.752	1.268
	L(3,4)	1.392	0.996	0.178	0.796	1.274
VIII	L(4,5)	1.392	0.995	0.178	0.793	1.274
	L(5,6)	1.394	0.989	0.173	0.746	1.267
	L(6,7)	1.400	0.963	0.161	0.622	1.246
VIII		1.388	1.000	0.190	0.909	1.293

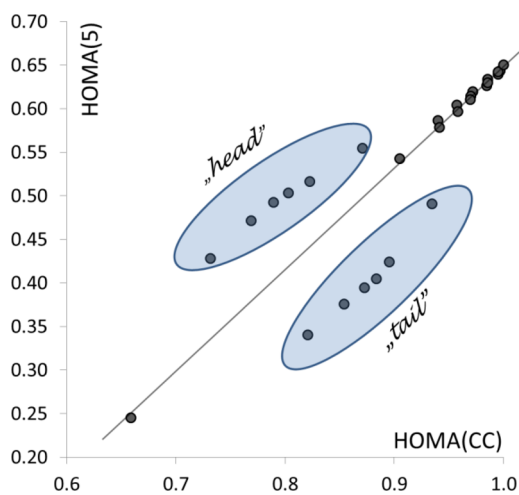
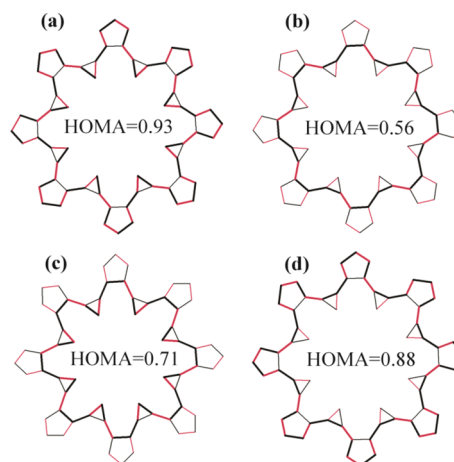


Figure 10. Scatter plot of HOMA index for five-membered rings and HOMA index for I bonds.

considered for the graph (see Figure 11, paths are marked with bold lines), it is possible to investigate which of the four paths is of highest π -electron delocalization. One may notice that the longest path (a) is the one of highest aromaticity (HOMA equals 0.930). Path b, being a “negative” of path a is constructed in such manner to make the closed path without using any of the edges of path a except of the edges corresponding to linking bond that are crucial for closed path construction, is the one that is least aromatic (HOMA = 0.560).

When considering the weighted-edges of the graph (black and red lines denoting single and double bonds, respectively), one may notice that the longest path of highest π -electron delocalization is the one that consists of conjugated formally single and double bonds. Interestingly, paths of the same pattern for II–VII are the ones of the highest π -electron delocalization, despite the corresponding paths in these systems

Figure 11. Edge weighted graph (black color denotes formally single bonds and red formally double bonds; bold lines denote paths) with closed π -electron delocalization paths of D_{sh} symmetry.

are not closed (as in the system VIII). When we consider “head” and “tail” units of systems II–VII, it appears that the local π -electron delocalization is the lowest in comparison to internal rings in these systems. It is worth noting that similar observations have previously been made for acenes,⁴³ systems of quite different topology in comparison to polycalicycenes. In the case of polycalicycenes this observation stems from the fact that the global π -electron delocalization of “head” and “tail” units is the one that is the most “perturbed” in comparison to calicycene units in VIII. As distinct from “head” and “tail” units, for internal calicycene units in II–VII, the pattern of global π -electron delocalization is closer to the pattern present in system VIII.

CONCLUSIONS

In this computational study, properties of planar poly-1,7-[N]calicycenes that consist of two to eight calicycene moieties were investigated. Direct relationship between local and global π -electron delocalization was found. For three- and five-membered rings of calicycene units and for bonds linking them, it was shown that the longer the polycalicycene chain, the greater the local π -electron delocalization in its inner part. Such observation results from the additional polarization of inner calicycene units by the electric dipoles of their neighboring counterparts. The comparison of polycalicycene with an isolated calicycene molecule exposed on an external electric field confirms such conclusion. Additionally, straightforward relations between the value of electric field applied and aromaticity of rings in calicycene, length of the bond connecting them, and dipole moment of a molecule were found. The presence of electric field also affects the total energy of the molecule such that the system is the least stable when the π -electron transfer between the rings is of the lowest degree ($4n + 1$ formal state). With the use of graph theory, it was also shown that for poly-1,7-[8]calicycene, the closed graph path consisting of conjugated single and double bonds is the one of highest π -electron delocalization. It is also very important to emphasize that for two series of rings, namely, three- and five-membered, it was shown that aromaticity is at least a two-dimensional phenomenon and for 99% data variance recovery three principal components are needed.

■ COMPUTATIONAL METHODS SECTION

The geometries of the systems I–VIII were optimized without any symmetry constraints at the B3LYP/6-311++G(d,p)^{44–48} level of theory. The frequency analysis was performed at the same level of theory. No imaginary frequencies were found for all but one system, that is, VII, for which one imaginary frequency of 36i cm⁻¹ corresponds to an out-of-plane vibration. Note, however, that frequencies of low magnitude (of absolute value less than 100 cm⁻¹) should be neglected since they are attributed to numerical noise, and thus, we consider the case of VII a minimum.^{49–51} Both, geometry optimization and frequency analysis computations in this study were carried out using Gaussian 09 program.⁵² For the optimized structures, an analysis of electron density distribution in the framework of quantum theory of atoms in molecules (QTAIM)³⁸ was performed with AIMAll program.⁵³

Furthermore, to fully understand the phenomenon of π -electron delocalization in poly-1,7-[N]calicenes, the calicene structure was optimized at the B3LYP/6-311++G(d,p)^{44–48} level of theory, in the presence of an electric field parallel to the axis of rotation of the calicene molecule. The value of electric field applied was from the interval –0.025 to 0.025 au. For the (calicene)₃ system consisting of three calicene units (Figure 9), partial optimization was carried out (distances shown in Figure 9 were frozen). In this case, the CAM-B3LYP⁵⁴ functional in conjunction with 6-311++G(d,p)⁴⁸ was applied. The calculations were performed with use of Gaussian09 program.⁵²

To describe aromaticity of the systems under investigation several aromaticity indices were applied. The first one, HOMA (harmonic oscillator model of aromaticity),^{27,28} is based on lengths of bonds forming a ring. For a ring that consists of CC bonds only, the following expression can be applied:

$$\text{HOMA} = 1 - \frac{1}{n} \alpha_{\text{CC}} \sum_{i=1}^n (R_{\text{opt,CC}} - R_i)^2 \quad (1)$$

where n represents the number of atoms forming a ring, α_{CC} is a normalization constant, $R_{\text{opt,CC}}$ denotes an optimal bond length in an aromatic system ($R_{\text{opt,CC}} = 1.388 \text{ \AA}$), and finally, R_i is the i th bond length.

HOMA can also be written as³⁷

$$\text{HOMA} = 1 - \text{EN} - \text{GEO} \quad (2)$$

where EN can be expressed as

$$\text{EN} = f \alpha_{\text{CC}} (R_{\text{opt,CC}} - R_{\text{av}})^2 \quad (3)$$

where $f = \text{sgn}(R_{\text{av}} - R_{\text{opt,CC}})$. The term EN is connected with the bond length change in comparison to the $R_{\text{opt,CC}}$ value. GEO can be defined with the equation

$$\text{GEO} = \frac{1}{n} \alpha_{\text{CC}} \sum_{i=1}^n (R_{\text{av}} - R_i)^2 \quad (4)$$

The GEO term describes the bond length alternation, that is, the difference between the length of the i th bond and the average bond length.

An aromatic fluctuation index (FLU)³² is another aromaticity descriptor used in the study. FLU is based on two-center delocalization indices. For single-determinant closed-shell wave functions, the delocalization index of atoms A and B is defined as^{24,25}

$$\delta(A, B) = 4 \sum_{i,j}^{N/2} S_{ij}(A) S_{ij}(B) \quad (5)$$

The sums in eq 5 run over $N/2$ occupied molecular orbitals. $S_{ij}(A)$ denotes the overlap of orbitals i and j within the basin of an atom A. FLU equals³²

$$\text{FLU} = \frac{1}{n} \sum_{A-B}^{\text{RING}} \left[\left(\frac{V(B)}{V(A)} \right)^\alpha \left(\frac{\delta(A, B) - \delta_{\text{ref}}(A, B)}{\delta_{\text{ref}}(A, B)} \right) \right]^2 \quad (6)$$

where n denotes the number of atoms forming a ring and the sum runs over all pairs of atoms A and B that are adjacent in the ring. For rings that consist of C atoms, only $\delta_{\text{ref}}(A, B)$ is the two-center delocalization index of adjacent atoms forming a benzene ring ($\delta_{\text{ref}}(C, C) = 1.389e$ at B3LYP/6-311++G(d,p) level of theory). $V(A)$ is a global delocalization of the atom A given by the formula

$$V(A) = \sum_{B \neq A} \delta(A, B) \quad (7)$$

Finally, α is a function that makes first parentheses of eq 6 equal to or greater than 1 and can be written as

$$\alpha = \text{sgn}[V(B) - V(A)] \quad (8)$$

Another aromaticity measure that was applied in the study is EL,³¹ an index based on bond ellipticity that is defined as²⁶

$$\varepsilon = \frac{\lambda_1}{\lambda_2} - 1 \quad (9)$$

where λ_1 and λ_2 are negative Hessian eigenvalues of electron density at the bond critical point (BCP). Their quotient describes the bond cross-section ellipticity. EL can be defined with the following equation:³¹

$$\text{EL} = 1 - \frac{c}{n} \sum_{i=1}^n |\varepsilon_i - \varepsilon_{\text{ref}}| \quad (10)$$

where c is a normalization constant, n denotes the number of atoms forming a ring, ε_i is the ellipticity of the i th bond, and finally ε_{ref} is the ellipticity of the CC bond in benzene (computed at the same level of theory as the system under study).

NICS (nucleus independent chemical shifts)²⁹ were applied as indicators of aromaticity based on magnetic properties. NICS(0)_{iso}²⁹ is the negative value of the shielding constant computed at the ring center. Other types of NICS applied were as follows: NICS(1)_{iso},³⁰ computed 1 Å above the ring center, and NICS(1)_{zzz},³³ the NICS(1)_{iso} component that is perpendicular to the ring plane (if the magnetic field applied is perpendicular to the ring). However, it should be pointed out that for small (three-membered) rings, NICS values may be unreliable because the NICS tensor is strongly affected by the σ contributions.^{55,56}

Additionally, to verify whether they follow same trends as aromaticity indices, several QTAIM parameters, namely, electron density (ρ), kinetic (G), potential (V), and total energy density (H) in ring critical points (RCPs),⁵⁷ were studied. To fully understand interrelations underlying indications of various aromaticity measures used in the study, the principal component analysis (PCA)⁴¹ was applied. This statistical method allows us to reveal the components (orthogonal vectors) that are able to describe a certain percentage of variance in the data and thus may lead to significant data reduction. Moreover, to fully describe the π -electron delocalization of systems investigated, the graph theory was applied.⁴²

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01441.

Cartesian coordinates, energies of all structures optimized, values of aromaticity descriptors used in the study, energetic parameters of the reaction of polycalicyene formation from calicene units, and composition of first principal components for each case of principal component analysis performed in the study (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: justyna@uni.lodz.pl.

Notes

The authors declare no competing financial interest.

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