Maejo Int. J. Sci. Technol. **2015**, 9(*01*), 21-31

Maejo International
Journal of Science and Technology

ISSN 1905-7873
Available online at www.mijst.mju.ac.th

Full Paper

Aromaticity of a series of poly-2,7-[N]calicenes

Thawalrat Ratanadachanakin [1,*] and Willard E. Collier [2]

[1] Faculty of Science, Maejo University, Sansai, Chiang Mai, 50290, Thailand
[2] Department of Chemistry, College of Arts and Sciences, Tuskegee University, Tuskegee, AL, 36088, USA

* Corresponding author, e-mail: thawalrat@mju.ac.th; fax: 66 5387 3548; tel.: 668 7504 3314

Received: 1 July 2014 / Accepted: 10 February 2015 / Published: 12 February 2015

Abstract: The nucleus independent chemical shift (NICS) criterion of aromaticity is used to evaluate the aromaticity of a series of poly-2,7-[N]calicenes. The geometry and NICS values of all poly-2,7-[N]calicenes and reference molecules (calicene, bicalicene, benzene, cyclopentadienyl anion and cyclopropenyl cation) are evaluated at the B3LYP/6-31G(d,p) level of computational theory. The NICS data indicate that all poly-2,7-[N]calicenes studied are aromatic, and aromaticity increases as the number of calicene units (N) increases.

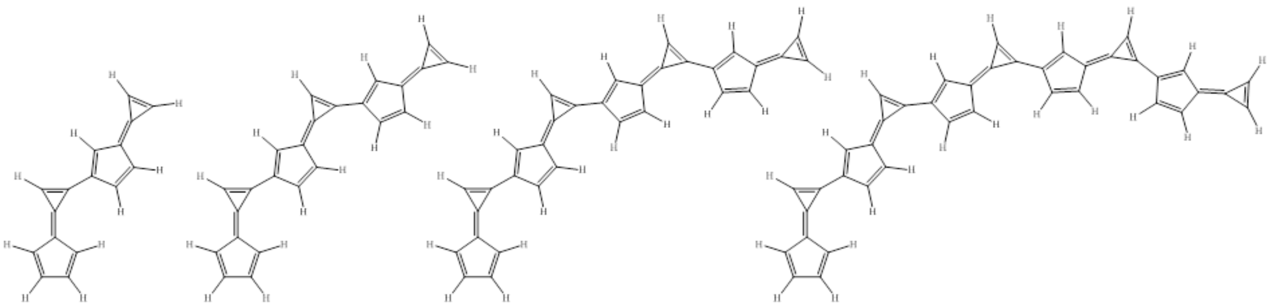
Keywords: polycalicenes, aromaticity, nucleus independent chemical shift, B3LYP

INTRODUCTION

Aromaticity is one of the foundational concepts in chemistry, but after almost 150 years of research, aromaticity still elicits spirited debates and has yet to be definitively defined [1-3]. Many criteria of aromaticity have been proposed such as chemical reactivity, aromatic stabilisation energy, bond length equalisation and various magnetic properties such as ^{1}H chemical shift, but no criterion has been accepted to be definitive [4-6]. Some lament the lack of agreement, but as pointed out by others this inability to reach a consensus has spurred research and led to many discoveries.

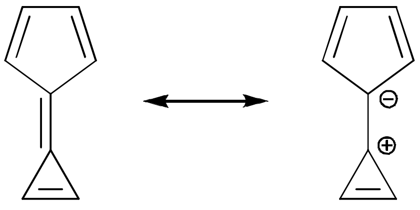
While benzene is the archetypal aromatic molecule, non-benzenoid aromatic compounds are intrinsically interesting and provide insight into the scope of aromatic character. The aromaticities of a novel series of poly-2,7-[N]calicenes (**1-4**, Figure 1), where 2,7 designates the location of the bond between calicene monomers and [N] is the number of calicene monomers, are investigated in this paper**.** Poly-2,7-[N]calicenes **1-4**, having N values of 2, 3, 4 and 5 respectively, have not been synthesised.

Poly-2,7-[N]calicenes are polymers of calicene (**5**, Figures 2 and 3), also known as triapentafulvalene. Calicene is frequently mentioned in organic chemistry textbooks as an aromatic molecule due to its dipolar resonance form (**5b**, Figure 2). With 4n + 2 π electrons in both of its five-membered ring (6 electrons) and three-membered ring (2 electrons), **5b** is expected to be the major contributor to the electronic structure of calicene. If **5b** is a major contributor, **5** would be expected to have a large dipole moment due to the dipolar character of **5b**. Intriguingly, calicene has never been synthesised, but substituted calicenes such as 2,3-dicyano-5,6-diphenylcalicene and 1,2,3,4-tetrachloro-5,6-diphenylcalicene are known and have large dipole moments [7, 8]. Even more surprisingly, bicalicene (**6**, Figure 3), a cyclic dimer of calicene with a 16-π peripheral electron system and expected to be anti-aromatic according to the 4n + 2 aromatic rule, was synthesised and characterised to be aromatic [9, 10].



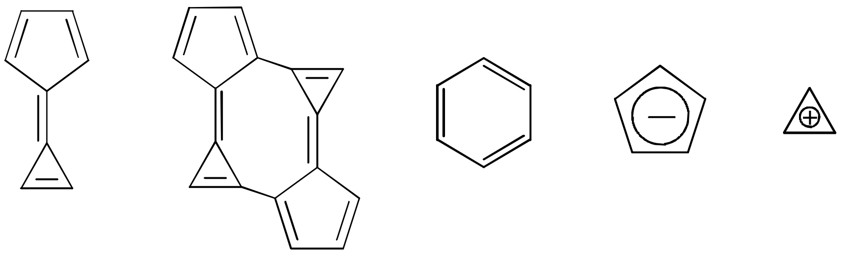
1 **2** **3** **4**

Figure 1. A series of poly-2,7-[N]calicenes



5a **5b**

Figure 2. Two main resonance forms of calicene (**5**)



5 **6** **7** **8** **9**

Figure 3. Reference molecules used in this study

This work is a continuation of previous investigations into the structure and aromaticity of various polycalicene families that result from different bonding motifs between the calicene monomers [11-12]. The poly-2,7-[N]calicenes are only one example of the rich variety of molecules that can be constructed from calicene building blocks. Polycalicenes are an unexplored region of chemical space, and the possibility that some polycalicenes are non-benzenoid aromatic molecules is inherently fascinating. Thus, the aromaticities of poly-2,7-[N]calicenes are evaluated in this paper using Schleyer's nucleus independent chemical shifts (NICS) [13]. The NICS values of calicene (**5**), bicalicene (**6**), benzene (**7**), cyclopentadienyl anion (**8**) and cyclopropenyl cation (**9**) (Figure 3) are calculated as references.

METHODS

The geometries of poly-2,7-[N]calicenes (**1-4**) were optimised using the density functional theory method composed of B3LYP functional [14, 15] and 6-31G(d,p) basis set [16, 17]. Harmonic vibrational frequency calculations were performed at the same level for all molecules to confirm that the molecules are of minimum energy conformations. NICS, defined as the negative of the calculated isotropic shielding [13], were evaluated at selected points (Figure 4). NICS(0) values (z=0) were calculated at points located at the centre (non-weighted average of ring atom coordinates) of the three-membered rings (cpro) and five-membered rings (cpent), and in the plane of each ring. NICS(1) values (z=1) were calculated at 1 Å above the NICS(0) point located at the ring centre and in the molecular plane of each ring. The geometries of all reference molecules, viz. calicene (**5**), bicalicene (**6**), benzene (**7**), cyclopenta-dienyl anion (**8**) and cyclopropenyl cation (**9**), were optimised at the same level of computational theory. NICS(0) and NICS(1) values for the reference molecules were calculated for comparison with the NICS results of **1-4**. All calculations were carried out using the Gaussian 09 suite of quantum mechanical programmes [18].

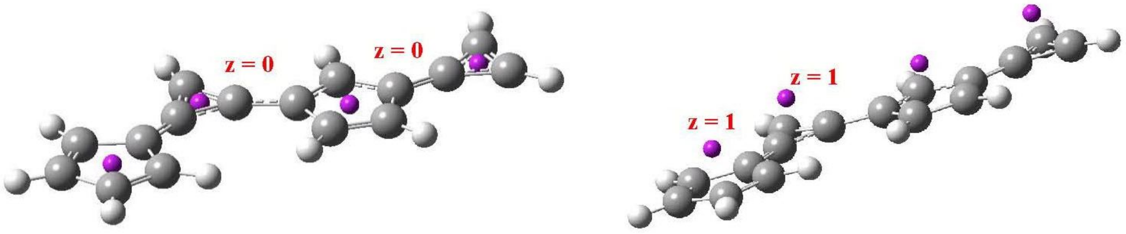


Figure 4. Location of NICS points, z=0 and z=1, for poly-2,7-[2]calicene (**1**)

RESULTS AND DISCUSSION

NICS Criterion of Aromaticity

NICS are a simple and robust criterion of aromaticity [13, 19]. NICS values are defined as the negative of the absolute magnetic shieldings computed at the 'ring centres (non-weighted mean of the heavy atom coordinates)'. Initially, NICS values were calculated only for points in the plane of the ring, designated as NICS(0) [13]. Negative NICS values indicate aromaticity and positive NICS values indicate anti-aromaticity. Since its introduction in 1996, there have been many refinements to the NICS method. Due to concerns over σ-electron contribution, it was proposed that NICS values be calculated 0.5 Å above the ring centre [20]. Next, NICS values are calculated 1 Å above the ring centre to further reduce the σ-electron contribution and are referred to as NICS(1) [21]. Further refinements have been proposed [20, 22, 23], such as separating the NICS values into σ- and π-electron contributions [20], but these 'refinements' detract from the simplicity of the original NICS method. Apart from the simplicity factor, the reliability of some of the latest refinements (e.g. NICS scan) [24] has been questioned.

Qualitative assignment of aromaticity is simple using NICS values, but quantitatively assessing the aromaticity is more complicated. Generally, the more negative the NICS value is, the more aromatic the system becomes. However, ring size and electron density also play a major role. Because of these concerns we always include, as reference molecules, well-known aromatic molecules (for example benzene) and, more importantly, aromatic molecules that are similar to the molecules under evaluation.

Despite its widespread use, some have questioned the reliability and even the fundamental wisdom of assessing aromaticity using the NICS criterion [25]. However, we have used the NICS criterion of aromaticity extensively and have refuted one purported failure of the NICS method touted by its critics [11]. We maintain that NICS(0) and NICS(1) values alone are a reliable and simple method of assessing aromaticity without resorting to complicated and arbitrary refinements. This study, therefore, focuses on the NICS(0) and NICS(1) values of the poly-2,7-[N]calicenes (**1-4**).

Poly-2,7-[N]calicene Ring Designations

Each poly-2,7-[N]calicene contains two or more calicene subunits that are numbered as illustrated in Figure 5 for the longest poly-2,7-[N]calicene studied, poly-2,7-[5]calicene (**4**). The calicene subunit that is bonded by its three-membered ring to the five-membered ring of the next calicene subunit is designated the first calicene subunit. The first calicene subunit is identified by no prime, the second calicene subunit by one prime (i.e. '), the third calicene subunit by two primes (i.e. "), and the progression continues as each calicene subunit is added. In addition, each calicene subunit has a three-membered ring (cpro) and a five-membered ring (cpent), so when combined, the numbering scheme and ring designation allows each ring to be identified uniquely. It is noted that when all three-membered rings are collectively described, cpro is used, but when three-membered rings are individually distinguished, cpro designates the three-membered ring of the first calicene subunit. Likewise when all five-membered rings are collectively described, cpent is used, but when five-membered rings are individually distinguished, cpent designates the five-membered ring of the first calicene subunit.

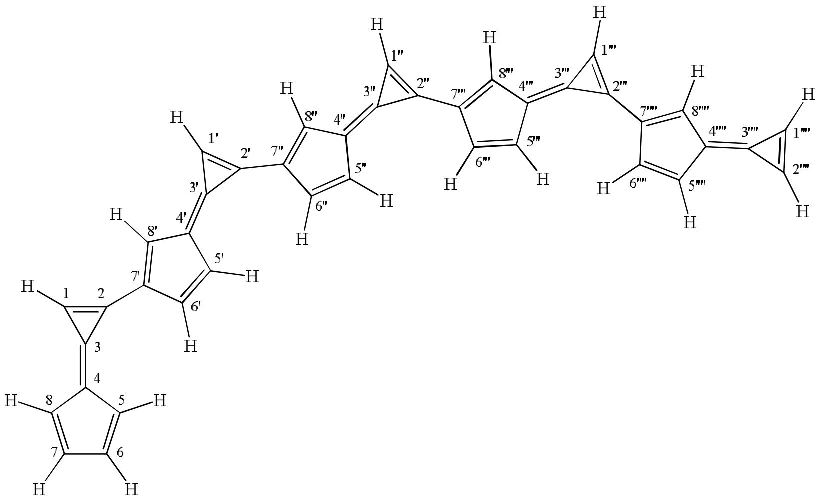


Figure 5. Numbering scheme of poly-2,7-[N]calicenes (**1-4**), illustrated by poly-2,7-[5]calicene (**4**)

Basis Set Choice

The calicene subunits of poly-2,7-[N]calicenes (**1-4**) are expected to have significant dipolar character with a five-membered ring that has significant cyclopentadienyl anion character and a three-membered ring that has significant cyclopropenyl cation character (Figure 2). Diffuse functions are recommended for calculations involving anions; therefore, it is best to use the larger 6-31+G(d,p) basis set that includes diffuse functions on the second row atoms [26]. Poly-2,7-[N]calicenes **1-3** were indeed studied using the 6-31+G(d,p) basis set; however, poly-2,7-[5]calicene (**4**) could not be optimised using the 6-31+G(d,p) basis set. We have consistently found that calculations involving polycalicene molecules (even those with different bonding motifs) as large as poly-2,7-[5]calicene (**4**) or larger using the 6-31+G(d,p) basis set generate a numerical error [11-12]. To demonstrate the reliability of the 6-31G(d,p) NICS data, we have included the B3LYP/6-31+G(d,p) NICS(0) and NICS(1) data for poly-2,7-[N]calicenes **1-3** in Table 1 and the same data for reference molecules **5-9** in Table 2.

Table 1. B3LYP/6-31+G(d,p) NICS(0) and NICS(1) data for poly-2,7-[N]calicenes (**1-3**)

Ring	**NICS(0) (ppm)**				**NICS(1) (ppm)**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
cpro	-22.9	-23.2	-23.4		-7.4	-7.5	-7.6	
cpro'	-21.2	-23.4	-23.8		-7.9	-8.1	-8.2	
cpro"		-21.5	-23.8			-8.3	-8.5	
cpro"'			-21.7				-8.6	
cpro""								
cpent	-5.6	-6.1	-6.6		-5.9	-6.2	-6.5	
cpent'	-4.7	-5.7	-6.2		-5.6	-6.2	-6.6	
cpent"		-4.8	-5.8			-5.6	-6.4	
cpent"'			-4.9				-5.8	
cpent""								

Table 2. B3LYP/6-31+G(d,p) NICS(0) and NICS(1) data for reference molecules (**5-9**)

Molecule		**Ring**	**NICS(0) (ppm)**	**NICS(1) (ppm)**
Calicene	**5**	Cpro	-20.5	-6.9
		Cpent	-4.5	-5.1
Bicalicene	**6**	Cpro	-23.3	-7.5
		Cpent	-4.7	-5.7
Benzene	**7**	Chex*	-8.1	-10.2
Cyclopentadienyl anion	**8**	Cpent	-12.8	-9.6
Cyclopropenyl cation	**9**	Cpro	-22.4	-14.5

* = six-membered ring

These data have been included to show that while the absolute values of the NICS data are different, essentially every trend (to be discussed) using the 6-31G(d,p) NICS data (Tables 3 and 4) is also found in the 6-31+G(d,p) NICS data in Tables 1 and 2. This validates the reliability of using the 6-31G(d,p) NICS data compared to the 6-31+G(d,p) NICS data. Therefore, the discussion will only focus on the B3LYP/6-31G(d,p) NICS(0) and NICS(1) data because those results are complete and more detailed comparisons can be made.

B3LYP/6-31G(d,p) NICS Data

The B3LYP/6-31G(d,p) NICS(0) and NICS(1) data for poly-2,7-[N]calicenes (**1-4**) are detailed in Table 3 and the same data for reference molecules (**5-9**) are listed in Table 4.

Table 3. B3LYP/6-31G(d,p) NICS(0) and NICS(1) data for poly-2,7-[N]calicenes (**1-4**)

Ring	**NICS(0) (ppm)**				**NICS(1) (ppm)**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
cpro	-23.5	-24.0	-24.3	-24.4	-7.9	-8.1	-8.2	-8.2
cpro'	-22.0	-24.0	-24.5	-24.6	-8.3	-8.6	-8.8	-8.9
cpro"		-22.2	-24.3	-24.7		-8.7	-9.0	-9.1
cpro"'			-22.4	-24.3			-8.9	-9.1
cpro""				-22.4				-9.0
cpent	-7.2	-7.7	-8.2	-8.3	-7.0	-7.3	-7.6	-7.7
cpent'	-6.0	-7.1	-7.6	-7.9	-6.6	-7.3	-7.7	-7.8
cpent"		-6.0	-7.2	-7.7		-6.7	-7.5	-7.8
cpent"'			-6.0	-7.2			-6.8	-7.5
cpent""				-6.2				-6.9

Table 4. B3LYP/6-31G(d,p) NICS(0) and NICS(1) data for reference molecules (**5-9**)

Molecule		**Ring**	**NICS(0) (ppm)**	**NICS(1) (ppm)**
Calicene	**5**	Cpro	-21.6	-7.6
		Cpent	-6.1	-6.4
Bicalicene	**6**	Cpro	-23.9	-8.0
		Cpent	-6.0	-6.8
Benzene	**7**	Chex*	-9.8	-11.3
Cyclopentadienyl anion	**8**	Cpent	-17.5	-12.5
Cyclopropenyl cation	**9**	Cpro	-22.4	-14.4

* = six-membered ring

The first and most notable overall trend revealed by the NICS results in Table 3 is that poly-2,7-[N]calicenes (**1-4**) are all aromatic according to the NICS criterion of aromaticity. All NICS values detailed in Table 3, both NICS(0) and NICS(1), are negative.

Before any discussion of how the aromaticity of the poly-2,7-[N]calicene varies with the length of the molecule and in particular how the aromaticity of the rings making up each molecule varies among **1-4**, it is logical to compare and contrast the NICS values of the reference molecules (Table 4) among themselves and how the NICS values of **1-4** compare to the reference molecules.

Benzene (**7**) is the archetypal aromatic molecule with an NICS(0) value of -9.8 ppm and NICS(1) value of -11.3 ppm and is included for completeness and illustration of the NICS method. However, none of the rings in the poly-2,7-[N]calicenes are benzene-like; instead, the rings are either three-membered or five-membered. The cyclopentadienyl anion (**8**) and cyclopropenyl cation (**9**) are more appropriate reference molecules, especially since the poly-2,7-[N]calicenes are expected to have significant charge separation.

The NICS(0) and NICS(1) values of cyclopentadienyl anion (**8**) (-17.5 ppm and -12.5 ppm respectively) are significantly lower than all cpent NICS(0) and NICS(1) values of **1-4**. This indicates that all cpent rings in **1-4** are significantly less aromatic than the cyclopentadienyl anion. This is reasonable since it is not expected that **1-4** would have complete charge separation between the cpro and cpent rings.

The NICS(0) value of cyclopropenyl cation (**9**) (-22.4 ppm) is higher than all the cpro NICS(0) values of **1-4** except for the cpro' NICS(0) of **1** (-22.0 ppm) and cpro'' NICS(0) of **2** (-22.2 ppm). These results indicate that the cpro rings of **1-4** are as aromatic as the cyclopropenyl cation or in some cases even more aromatic. However, the NICS(1) value of **9** (-14.4 ppm) is significantly lower than the cpro NICS(1) values of **1-4** (all between -7.9 to -9.1 ppm). The cpro NICS(1) data indicate that the cpro rings of **1-4** are significantly less aromatic than the cyclopropenyl cation. The discrepancy between the cpro NICS(0) and NICS(1) data of **1-4** can be explained since NICS(0) values are known to be influenced by the σ-electrons and the extended conjugation found in **1-4** would distort the molecular framework and the σ-electrons. As mentioned earlier, NICS(1) values are regarded as more reliable since they are mainly influenced by the π-electrons.

While the cyclopentadienyl anion and the cyclopropenyl cation are better reference molecules than benzene, they are still isolated small ring molecules and do not fully reflect the molecular environment of the poly-2,7-[N]calicenes. Two better reference molecules are calicene (**5**) and bicalicene (**6**). These two molecules are expected to have significant dipolar character with a five-membered ring that has significant cyclopentadienyl anion character and a three-membered ring that has significant cyclopropenyl cation character, just as expected for poly-2,7-[N]calicenes (**1-4**).

The case for **1-4** being aromatic is strengthened because their NICS values are more negative than almost all of their corresponding NICS values in calicene (**5**). For example, **5** has a cpro NICS(0) of -21.6 ppm, compared to -22.0 ppm for cpro' of **1**, the highest NICS(0) value for all the cpro rings (cpro, cpro', cpro'', cpro''' and cpro'''') of **1-4**. The cpro NICS(1) value of **5** (-7.6 ppm) is also higher than the highest cpro NICS(1) value of **1-4** (-7.9 ppm) found in cpro of **1**. The cpent NICS(0) and NICS(1) values of **5** (-6.1 ppm and -6.4 ppm respectively) are higher than all but the respective terminal cpent NICS(0) values of **1-3** (all -6.0 ppm).

The most telling comparison is between the NICS(0) and NICS(1) values of **1-4** and those of bicalicene (**6**), because bicalicene was shown to be aromatic experimentally and a recent theoretical examination confirms the aromaticity of bicalicene [27]. Considering the cpro NICS results, only cpro **1** and the terminal cpro rings of **1-4** have higher NICS(0) values than the -23.9 ppm for the cpro of **6**. Even more important, the cpro NICS(1) of **6** (-8.0 ppm) is lower than only one of the total cpro NICS(1) values for **1-4**, the NICS(1) value of cpro **1** (-7.9 ppm). The cpent NICS(0) of **6** (-6.0

ppm) is higher than all but the terminal cpent NICS(0) values of **1-3** (all -6.0 ppm). Likewise, the cpent NICS(1) of **6** (-6.8ppm) is higher than all but the terminal cpent NICS(1) values of **1-3** (-6.6 ppm, -6.7 ppm and -6.8 ppm respectively).

The second main trend revealed by the data is that the molecules become more aromatic as the length of the poly-2,7-[N]calicene increases. This trend is easily confirmed by comparing either the NICS(0) or NICS(1) values of a specific ring across all poly-2,7-[N]calicenes containing that ring. All poly-2,7-[N]calicenes **1-4** have cpent, cpro, cpent′, and cpro′ rings so these are the most important rings to compare.

Looking at the first ring in **1-4**, the cpent NICS(0) values for (-7.2 ppm, -7.7 ppm, -8.2 ppm and -8.3 ppm respectively) and the cpent NICS(1) values (-7.0 ppm, -7.3 ppm, -7.6 ppm and -7.7 ppm respectively) all increase as the length of the molecule increases. The data for the second ring in **1-4** continues the trend with cpro NICS(0) values of -23.5 ppm, -24.0 ppm, -24.3 ppm and -24.4 ppm respectively, and cpro NICS(1) values of -7.9 ppm, -8.1 ppm, -8.2 ppm and -8.2 ppm respectively. The increase in aromaticity with the length of the molecule is also evident when comparing the second calicene subunit of **1-4,** with cpent′ NICS(0) values of -6.0 ppm, -7.1 ppm, -7.6 ppm and -7.9 ppm respectively, and cpent′ NICS(1) values of -6.6 ppm, -7.3 ppm, -7.7 ppm and -7.8 ppm respectively. The cpro′ NICS(0) values for **1-4** of -22.0 ppm, -24.0 ppm, -24.5 ppm and -24.6 ppm respectively, and the cpro′ NICS(1) values of -8.3 ppm, -8.6 ppm, -8.8 ppm and -8.9 ppm respectively, again reveal increasing aromaticity as the length of molecule increases.

The trend of increasing aromaticity as the length of the molecule increases also holds for the rings shared by the longer poly-2,7-[N]calicenes (**2-4**). The cpent'' NICS(0) values for **2-4** of -6.0 ppm, -7.2 ppm and -7.7 ppm respectively, and cpent'' NICS(1) values of -6.7 ppm, -7.5 ppm and -7.8 ppm respectively, all reflect the trend of increasing aromaticity as the length of the molecule increases. Likewise this trend is found in the cpro'' NICS(0) values (-22.2 ppm, -24.3 ppm and -24.7 ppm respectively) and the cpro'' NICS(1) values for **2-4** (-8.7 ppm, -9.0 ppm and -9.1 ppm respectively).

Even the rings shared by the longest poly-2,7-[N]calicenes (**3-4**) reflect the trend of increasing aromaticity as the length of the molecule increases, as shown by the cpent''' NICS(0) values (-6.0 ppm and -7.2 ppm respectively) and cpent''' NICS(1) values for **3-4** (-6.8 ppm and -7.5 ppm respectively. This trend is also found in the cpro'''NICS(0) values (-22.2 ppm and -24.3 ppm respectively) and cpro''' NICS(1) values for **3-4** (-8.9 ppm and -9.1 ppm respectively).

The data detailed above confirm that poly-2,7-[N]calicene increases in aromaticity as the length of the molecule increases. The only exception to this trend is found for the cpro NICS(1) values of **3** and **4** that remain the same (-8.2 ppm).

One of the two minor trends that can be teased out from the data, but only by majority consensus, is that the terminal cpro and cpent rings of each poly-2,7-[N]calicene (**1-4**) are the least aromatic of all the cpro and cpent rings in that poly-2,7-[N]calicene. This conclusion is supported by all the cpro NICS(0) values for **1-4**; for example, the cpro'''' NICS(0) value of **4** is -22.4 ppm, compared to -24.4 ppm, -24.6 ppm, -24.7 ppm and -24.3 ppm for its other cpro NICS(0) values. The cpent NICS(0) values for **1-4** also reveal this trend; for example, the cpent'''' NICS(0) value of **4** is -6.2 ppm, compared to -8.3 ppm, -7.9 ppm, -7.7 ppm and -7.2 ppm for its other cpent NICS(0) values. Likewise, the cpent NICS(1) values for **1-4** support the conclusion that the terminal rings of each poly-2,7-[N]calicene are less aromatic than their counterparts; for example, the cpent''''

NICS(1) value of **4** is -6.9 ppm, compared to -7.7 ppm, -7.8 ppm, -7.8 ppm and -7.5 ppm for its other cpent NICS(1) values.

While the cpro NICS(0), cpent NICS(0) and cpent NICS(1) data support our conclusion that the terminal cpro and cpent rings of each poly-2,7-[N]calicene (**1-4**) are the least aromatic of all the cpro and cpent rings in that poly-2,7-[N]calicene, the cpro NICS(1) data contradict this conclusion. For example, the terminal cpro' of **1** has an NICS(1) value of -8.3 ppm while the cpro NICS(1) value is -7.9 ppm. Likewise the terminal cpro'' of **2** has an NICS(1) value of -8.7 ppm compared to -8.6 ppm for cpro' and -8.1 ppm for cpro of **2**. The terminal cpro''' of **3** has an NICS(1) value of -8.9 ppm that is less aromatic than its cpro'' at -9.0 ppm, but more aromatic than either the cpro' at -8.8 ppm or cpro at -8.2 ppm. Similar to **3**, the terminal cpro'''' has an NICS(1) value of -9.0 ppm, which is less aromatic than either its cpro''' or cpro'', both having an NICS(1) value of -9.1 ppm, but more aromatic than its cpro' at -8.9 ppm or cpro at -8.2 ppm. Note that as the length of the molecule increases, the cpro NICS(1) results become less of an exception to the trend that the terminal cpro and cpent rings of each poly-2,7-[N]calicene are the least aromatic of all the cpro and cpent rings in that poly-2,7-[N]calicene.

The second minor trend, by a slim majority of data and more correctly titled ‘emerging trend’, is that as the length of the molecule increases, the cpro and cpent rings near the middle of a poly-2,7-[N]calicene become more aromatic than their counterparts at either end of the same molecule. This emerging trend can be seen in the cpro NICS(0), cpro NICS(1) and cpent NICS(1) data. This trend is contradicted by the consistently decreasing cpent (cpent, cpent', cpent'', cpent''' and cpent'''') NICS(0) values for molecules **1-4**, for example -8.2 ppm, -7.6 ppm, -7.2 ppm and -6.0 ppm for cpent, cpent', cpent'' and cpent''' respectively of **3**. However, a closer examination of the cpent NICS(0) results shows tantalising evidence that the terminal cpent rings are becoming more negative at a slower rate than the middle cpent rings. It is predicted that if longer poly-2,7-[N]calicenes were studied, this trend of the cpro and cpent rings near the middle of a poly-2,7-[N]calicene being more aromatic than their respective counterparts in the same molecule would be confirmed. It is planned to investigate longer poly-2,7-[N]calicenes and the results obtained should resolve the validity of both minor trends described above.

CONCLUSIONS

The NICS data indicate that poly-2,7-[N]calicenes (**1-4**) are aromatic, and the aromaticity increases as the number of calicene units (N) increases. These results reveal that poly-2,7-[N]calicenes are a novel family of non-benzenoid aromatic molecules and therefore are intriguing synthetic targets.

ACKNOWLEDGEMENTS

The computer time for this research was provided by the Mississippi Centre for Supercomputing Research.

REFERENCES

1. D. Lloyd, “What is aromaticity?”, *J. Chem. Inf. Comput. Sci.*, **1996**, *36*, 442-447.
2. P. von Rague Schleyer and H. Jiao, “What is aromaticity?”, *Pure Appl. Chem.*, **1996**, *68*, 209-218.
3. A. T. Balaban, “Is aromaticity outmoded?”, *Pure Appl. Chem.*, **1980**, *52*, 1409-1429.

4. M. K. Cyranski, T. M. Krygowski, A. R. Katritzky and P. von Rague Schleyer, "To what extent can aromaticity be defined uniquely?", *J. Org. Chem.*, **2002**, *67*, 1333-1338.
5. T. M. Krygowski, M. K. Cyranski, Z. Czarnocki, G. Hafelinger and A. R. Katritzky, "Aromaticity: A theoretical concept of immense pratical importance", *Tetrahedron*, **2000**, *56*, 1783-1796.
6. V. I. Minkin, M. N. Glukhovtsev and B. Ya. Simkin, "Aromaticity and Antiaromaticity: Electronic and Structural Aspects", John Wiley and Sons, New York, **1994**.
7. B. Halton,"The fulvalenes", *Eur. J. Org. Chem.*, **2005**, *16*, 3391-3414.
8. A. Al-Dulayymi, X. Li and M. Neuenschwander, "Further synthetic attempts towards calicene", *Helv. Chim. Acta*, **2000**, *83*, 1633-1644.
9. Z. -i. Yoshida, "Novel pi systems possessing cyclopropenylidene moiety", *Pure Appl. Chem.*, **1982**, *54*, 1059-1074.
10. S. Yonedo, M. Shibata, S. Kida, Z. Yoshida, Y. Kai, K. Miki and N. Kasai, "A novel aromatic hydrocarbon with 16π-electron periphery: Cyclic bicalicene", *Angew. Chem. Int. Ed. Engl.*, **1984**, *23*, 63-64.
11. W. E. Collier, "A computational investigation of some polycalicenes as novel nonbenzenoid aromatic molecules and the strange case of the cyclopropenyl anion", *PhD Dissertation*, **2009**, Mississippi State University, USA.
12. W. E. Collier and T. Ratanadachanakin, "The Potential of Bandcalicenes as carbon dioxide hosts", *J. Interdiscipl. Networks*, **2013**, *2*(Sp. Iss.), 112-117.
13. P. von Rague Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, "Nucleus-independent chemical shifts: A simple and efficient aromaticity probe", *J. Am. Chem. Soc.*, **1996**, *118*, 6317-6318.
14. A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange", *J. Chem. Phys.*, **1993**, *98*, 5648-5652.
15. C. Lee, W. Yang and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", *Phys. Rev. B*, **1988**, *37*, 785-789.
16. W. J. Hehre, R. Ditchfield, R. F. Stewart and J. A. Pople, "Self-consistent molecular orbital methods. IV. Use of gaussian expansions of slater-type orbitals. Extension to second-row molecules", *J. Chem. Phys.*, **1970**, *52*, 2769-2773.
17. R. Ditchfield, W. J. Hehre and J. A. Pople, "Self-consistent molecular orbital methods. IX. An extended gaussian-type basis for molecular-orbital studies of organic molecules", *J. Chem. Phys.*, **1971**, *54*, 724-728.
18. 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, "Gaussian 09, Revision A.1", Gaussian Inc., Wallingford (CT), **2009**.

19. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. von Rague Schleyer, "Nucleus-independent chemical shifts (NICS) as an aromaticity criterion", *Chem. Rev.*, **2005**, *105*, 3842-3888.
20. P. von Rague Schleyer, K. Najafian, B. Kiran and H. Jiao, "Are oxocarbon dianions aromatic?", *J. Org. Chem.*, **2000**, *65*, 426-431.
21. P. von Rague Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin and O. L. Malkina, "An evaluation of the aromaticity of inorganic rings: Refined evidence from magnetic properties", *J. Am. Chem. Soc.*, **1997**, *119*, 12669-12670.
22. S. Noorizadeh and M. Dardab, "A new NICS-based aromaticity index; NICS rate", *Chem. Phys. Lett.*, **2010**, *493*, 376-380.
23. A. Stanger, "Nucleus-independent chemical shifts (NICS): Distance dependence and revised criteria for aromaticity and antiaromaticity", *J. Org. Chem.*, **2006**, *71*, 883-893.
24. P. Seal and S. Chakrabarti, "Is nucleus-independent chemical shift scan a reliable aromaticity index for planar heteroatomic ring systems?", *J. Phys. Chem. A*, **2007**, *111*, 9988-9994.
25. P. Lazzeretti, "Assessment of aromaticity via molecular response properties", *Phys. Chem. Chem. Phys.*, **2004**, *6*, 217-223.
26. T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. von Rague Schleyer, "Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li-F", *J. Comput. Chem.*, **1983**, *4*, 294-301.
27. W. P. Oziminski, M. Palusiak, J. Dominikowska, T. M. Krygowski, R. W. A. Havenith, C. M. Gibson and P. W. Fowler, "Capturing the elusive aromaticity of bicalicene", *Phys. Chem. Chem. Phys.*, **2013**, *15*, 3286-3293.