Organic & Supramolecular Chemistry

N,N- and N,O-6-membered Ring *peri*-Annelation in Naphthalene. Is it a Heteroring or merely a *peri*-Heterobridge?

Demeter Tzeli*^[a, b] and Petros G. Tsoungas*^[c]

The effect of *peri*-fusion on the aromaticity of 6-membered N–, O–, N,N–, N,N– and N,O-doped naphthalene derivatives has been studied via NICS-z, -xz, -xy, and -xyz scans employing DFT and MP2 calculations. The relative aromaticity of these structures was found to vary with the type of heteroring and the distance from the plane. Their corresponding ordering depends on the scan approaches. Accordingly, i) along the z axis at the center of the naphthalene **B** and **C** constituent rings, it is $1,8 > 2 > 7,9 \gg 4 > 6$, 5 > 3 (the most aromatic members are naphthalene and the N,O-derivative **8**), ii) along the x symmetry axis of naphthalene, it is 3 > 8,7 > 5 > 4 > 9 > 6 > 2 >

Introduction

Aromaticity, one of the fundamental concepts in chemistry, has been a long and strongly debated subject with a vast literature on both its physical significance and applications,^[1,2] largely explored in linear or angular ('kinked') (poly)cyclic aromatic hydrocarbons (PAHs).^[2-4] Condensed (or fused) polycyclic (hetero) aromatic compounds (P(H)ACs) have also shared an extensive research interest, thanks to their intriguing geometry features^[5-7] and diverse applications.^[8-11] In trying to quantify, thus, give a physical substance to the concept, various indices/ descriptors have been developed over the years, such as structural,^[12,13] magnetic,^[7,14,15] energetic,^[13] electronic^[16] and reactivity-based ones,^[17] to measure the degree of aromaticity of PAHs and their heterocyclic analogues.^[2,15,18-22] A succinct presentation^[23] and assessments^[18-26] of these indices have been reported.

[a] Prof. D. Tzeli Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, Athens 157 84, Greece E-mail: tzeli@chem.uoa.gr [b] Prof. D. Tzeli Theoretical and Physical Chemistry Institute National Hellenic Research Foundation 48 Vassileos Constantinou Ave., Athens 116 35, Greece [c] Dr. P. G. Tsoungas Department of Biochemistry Hellenic Pasteur Institute 127 Vas.Sofias Ave., Athens, GR-11521, Greece E-mail: pgt@otenet.gr pgt@pasteur.gr Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202004237

1 (the most aromatic one is a N-derivative 3) and iii) along the z axis, on the xy plane, it is 6>1>8>9>2>5>7>3>4 at z=0.8 Å and 1>2>8>9>6>7>5>3>4 at 2.4 Å (the most aromatic ones are the N,N,N-derivative 6 at 0.8 Å and naphthalene at 2.4 Å). Their relative magnetic anisotropy ordering remains virtually unaltered in all different approaches (z-, xz-, xy-, and xyz-scans), as does their aromaticity at z=2.4 Å. The σ component of the total density is dominant close to the plane while the π component picks up in significance with increasing distance from the plane. The *peri*-fused ring appears to be a heteroring not just a heterobridge.

Check for updates

Europe

European Chemical Societies Publishing

Annelation, most commonly benzo-annelation, may develop linearly or angularly onto an existing aromatic bicycle. It has been found that aromaticity of the ring directly attached to it, decreases in the former or increases in the latter case.^[2] Periannelated (or condensed) PAHs and their heterocyclic congeners have the peri positions of a naphthalene core as part of a (hetero)ring. Some well-known structures like phenalene, acenaphthene and pyrene have been a research theme for some time.^[27,28] Peri annelation (or fusion) introduces rigidity to a structure, causes its distortion^[29] and eventually deviation from planarity.^[30] The latter, as an inherent feature of an aromatic structure, can result from a variety of factors, steric hindrance at the periphery of the aromatic core, e.g., bulky substituents^[31] or ring strain^[32–34] being the most common ones. Ring strain, in particular, may arise from peri bridging as in pyrenes.^[35] 1,2- or 1,3-diazanaphthalenes (known as perimidines or peridazines), as well as their acenaphth(yl)ene hetero analogues are major members of the group of peri-annelated heterocycles.^[36] N-(and N,N-), O-(and N,O-) doped heterocycles exhibit diverse bio (pharmaco) logical profiles.^[37,38] Their peri-fused N,O- congeners, on the other hand, are much less known.^[36] Various approaches have been developed to estimate the aromaticity of N-(and N,N-), O-(and N,O-) heterorings (Figure 1), using a variety of indices, [15,39] the credibility of which has also been assessed.^[24,40] The aromaticity of azines^[41] and other 5- and 6-membered heterorings^[15,18,25,42,43] has been and still is a research theme. Intriguing features of the structure of peri-fused N,O- heterorings 3-9 (Figure 2), reflecting their reactivity profile, have been recently reported.[44] It is the implications of peri fusion on their structure that sparked our interest to explore their aromatic character.

Wiley Online Library





Figure 1. General representation of peri-annelated structures.



Figure 2. N-, N,N-, N,N,N-, O- and N,O- peri -annelated structures.

Results and Discussion

All structures were geometry optimized at the B3LYP^[45] and $MP2^{[46]}/6-311 + +G(d,p)^{[47]}$ levels of theory. Dipole moments, dipole electric field isotropic and anisotropic polarizability plots, magnetic isotropy and anisotropy contour plots and the Nucleus-Independent Chemical Shifts (NICS) indices^[7,40] were computed at both levels of theory, see Tables 1 and 3 and S1-S8 of SI. To avoid spurious interference from in-plane tensor components, NICS values have been computed above the ring, up to z=5 Å. The aromaticity has been explored by NICS-z, NICS-xy, NICS-xz and NICS-xyz-scan and magnetic anisotropy z, xz, xy and xyz-scan.^[48-52] The NICS-xy-scan identifies local and global ring currents in PAHs and predicts their properties both qualitatively and quantitatively. In addition, using naphthalene, as the core (building block) of 2-9, both relative NICS (ANICS) and magnetic anisotropy values were computed with respect to 1, i.e., the corresponding values of 1 were subtracted from those of 2-9. Thus, the effect of the peri ring on naphthalene was computed, highlighting its effect on the structures and leading to the aromaticity ordering of the series. The NMR shielding tensors have been computed with the Gauge-Independent Atomic Orbital (GIAO) method.^[53] All calculations were carried out via the Gaussian16 program.^[54]

Electron density distribution in heterocycles is affected by ring heteroatom(s). Their electronegativity, size and lone pairs cause changes in bond lengths and polarization of the σ -skeleton, leading to distortion and a non-uniform π density distribution.

Peri-fusion distorts the geometry of 3-9 (Figure 2) and further their reactivity profile.^[44] C atoms of the peri-fused ring in the parent structure 2 are replaced (in part or in full) by N and O heteroatoms in a varying arrangement, i.e., contiguously bonded, as in 4, 6 and 8, those one C unit apart, such as 5 and 9 and those with one heteroatom, like 3 and 7. The incorporation of N atoms into the A ring (Figure 2, 3-6) imparts strain into the C skeleton, enhanced further by partly replacing N by O (Figure 2, 7-9). Clearly, the above mentioned features of ring A heteroatom (s) modify the σ - and/or π -frame, triggering a deformation and ultimately their deviation from planarity.[55] The latter expectedly perturbs the aromatic character of the structures. Geometry changes (bond lengths and angles, *peri* H–H distance) have shown^[44] only a weak π perturbation but a notable σ - one of the structure. Dihedral angles^[44] reveal that 2, 5 and 7–9 are entirely planar, 3 and 4 are virtually planar (variation in the range of ca. 0.01–0.05°) and it is only 6 notably deviating from planarity of ca.1-6°. More revealing of the inherent strain are the bond angles of 2-9, particularly C_3 - C_{3a} - C_{9aa} and C_{3a} - C_{9aa} - C_{9a} in the fusion (L region) region with a deviation range from 1 of $1.4-4.1^{\circ}$ or $1.2-3.7^{\circ}$, respectively. More importantly, the latter shows a steeper orientation while the former one is more or less sensitive to the number and arrangement but not the nature of ring heteroatoms. Overall, a sharper fusion angle is observed in 3, 4, 7 and 8, a markedly larger in 5 and 6 whereas no change is found in 2 and 9.^[44] In other words, an "outward" stretching of their lower part and a corresponding "inward" compression of their upper one has been detected. It has been proposed^[44] that the hetero ring is virtually an unsaturated (e.g., enamine, hydrazone, imine, vinyl ether, oxime or imino ether) peri bridge, clamped onto the naphthalene scaffold. Heteroatoms in 4 and 8 are part of a hydrazine or a hydroxylamine entity, respectively. The facile rupture of the ring N–O bond in 8 lends sound experimental support^[56] for ring A inherent strain. 4 and 8, housing the masked hydrazine and oxime entities, appear to exhibit a "ring α -effect"-guided reactivity,^[44] consistent with preliminary experimental findings.

In discussing the aromaticity of the series, one should keep in mind that (a) it is a derivative concept of their structure profile (Figure 2) and (b) it will divulge a useful insight into their reactivity, mainly focused on selectivity. Moreover, their aromaticity cannot be sufficiently described by looking at each ring separately, given that π electron density is spread over the entire structure **or** *is it*? In any case, until a universally accepted definition of and a commonly agreed by all disciplines measurement for aromaticity are reached, it will remain a



notion aptly referred to …" like beauty, in the eyes of the beholder".^[15] "-The idea of NICS-scan was developed by many researchers.^[50-52] The NICS notion and its ability to be or not a measurable quantity has been criticized. NICS is affected by the electron distribution in the center and in the vicinity of the center of rings as well as ring size. The methodology used herein is suitable and safe to compute as it virtually covers the entire structure of rings of comparable size.^[57-59] NICS sensitivity to local currents, on the other hand, is not an issue here, as this is predominantly found in organometallics.^[60] Despite its criticism,^[61] NICS^[48-52] has been adopted as the aromaticity assessment technique of choice, in the present work. The NICS-xyz-scan is regarded as a technique providing information of



Figure 3. Dipole moment μ /Debye, dipole electric field isotropic polarizabilities (iso)/au, and anisotropic polarizabilities (aniso)/au for 1–9 at B3LYP (dotted lines, open points) and MP2(solid lines, solid points) /6-311 + +G-G(d,p) levels of theory.

value equal to that extracted from current density analysis methods, in more detail, in some cases.^[52]

Worth noting at this point is that it is *trends rather than actual changes* in the aromaticity features of **3**–**9** that will be contemplated throughout the ensuing discussion. Conceptually, the effects of *peri*-fusion on the aromaticity of the **3**–**9** series could be looked at by considering all core structure combinations AB + C, AC + B and BC + A rings. Naphthalene BC core is, however, considered as the reference building block for xyz-scans and structure profile of A as the *peri*-fusion heteroring. On the other hand, azanaphthalenes AC or AB rings, with **B** or **C** as their *peri*-fusion rings, respectively, are rather unsuitable as reference core structures for it is known^[41,62] that they lag behind their parent naphthalene in aromaticity.

Calculations of dipole moments, (an)isotropic polarizabilities, magnetic (an)isotropy and Nucleus-Independent Chemical Shifts (NICS), run by both DFT(B3LYP) and MP2 methodologies, gave quite similar results (see Tables 1–3, Figures 1–11, Tables S1–S11 and Figures S1–S16 of SI). Thus, in the paper mainly the MP2 data are provided, while the DFT data are given in SI.

Dipole electric field (an)isotropic polarizabilities and dipole moments: MP2 and DFT(B3LYP) dipole moments μ and dipole electric field isotropic and anisotropic polarizabilities are given Table S10 of SI and they are plotted in Figure 3. The good agreement of the two methodologies is observed in Figure 3.

The generally *ca.* 25% larger isotropic polarizabilities^[63] than their anisotropic rivals demonstrate similar trends. The most notable increase of about 29% is observed in 2. While not as suitable as anisotropy-based indices of aromaticity,^[64] polarizability-based ones do reflect on structure stability.^[65] Accordingly, an isotropic polarizability relative ordering for the series has been found to be $3 \ge 2 > 4 > 5 > 7 > 6 > 8 > 9 > 1$, com-



Figure 4. Magnetic anisotropy and NICS_{zz} values in the center of the rings A, B and C (Figure 1) along the z axis for 1–9 at MP2/6-311 + +G(d,p).





Figure 5. Magnetic anisotropy (Δ Anisotropy) and NICS_{zz} values (Δ NICS_{zz}) in the center of the rings B and C (Figure 1) along the z axis for 2–9 at MP2/6-311 + +G(d,p) with respect to 1.

Table 1. NICS _{zz} values and magnetic anisotropy(z) in the center of the rings A, B and C at the z axis (see Figure 1) for 1–9 at MP2/6-311 + +G(d,p).								
	NICS _{zz} A ^{a,b}	Bª	Bc	Ca	Cc			
1	-	-8.52	-11.02	-8.52	-11.02			
2	6.94	-6.31	-9.12	-8.28	-10.74			
3	7.61	-5.37	-7.96	-6.50	-8.60			
4	9.09	-5.74	-8.52	-6.94	-9.01			
5	8.86	-7.08	-9.46	-6.89	-8.83			
6	11.80	-7.27	-9.64	-6.84	-8.87			
7	7.45	-6.29	-8.82	-8.75	-10.45			
8	8.11	-6.49	-9.11	-9.19	-10.93			
9	8.55	-7.48	-9.81	-8.83	-10.40			
	Anisotropy(z)							
	Anisotroj	A ^{a,d}	$B^{e,d}$	$C^{e,d}$				
1		-	29.05	29.05				
2		23.39	24.54	27.26				
3		27.52	21.36	21.21				
4		29.11	21.61	21.81				
5		30.03	23.56	21.41				
6		30.97	23.56	21.15				
7		28.02	22.51	24.71				
8		26.48	23.68	25.70				
9		28.35	23.70	24.43				
$^{\rm a}$ At z=0 Å see Table S4 of SI. $^{\rm b}$ Highest antiaromaticity values. $^{\rm c}$ Highest								

aromaticity values, at $z = \sim 0.8$ Å, see Table S5 of SI. ^d Highest magnetic anisotropy. ^e At $z = \sim 1.2$ Å, see Table S6 of SI.

pared against a corresponding $3 > 4 > 5 \ge 6 \ge 2 > 7 > 8 > 9 > 1$ ordering for anisotropic polarizability (Table 9S of SI). In other words, the -N (N,N-, and N,N,N-) **3**-6 members, can be viewed as more stable than their O-(and N,O-) doped congeners **7**-9. The electric dipole moment, as a measure of a structure's

Table 2. NICSNICSAlignmetric and a state of the						
	NICS _{xz} $z = 0 \text{ Å and } x = \sim -2.5 \text{ Å}$	Anisotropy z=0 Å and x=0 Å				
1	-41.68	61.92				
2	-41.84	56.79				
3	-44.54	47.65				
4	-43.82	48.35				
5	-43.87	49.62				
6	-43.36	48.50				
7	-44.41	51.77				
8	-44.43	52.96				
9	-43.60	52.88				

overall polarity, shows an ordering of 8 > 5 > 6 > 3 > 9 > 7 > 2 > 4 > 1 (see Table 9S of SI), with values in the range 3.67–0.76 Debye. Interestingly, 2, 4, 7 and 9 have similar low dipole moments.

NICS_{zz} at the center of A, B and C rings: The most popular method for identifying the aromaticity of a ring is the calculation of the NICS value in the center of the ring. Initially, the descriptor was calculated on the plane, NICS(0), and then at a distance of 1 Å above it, NICS(1). The latter was considered as a better aromaticity descriptor. However, there is a dispute for the effectiveness of both NICS(0) and NICS(1) for multiple fused rings based on the π electron distribution over the entire structure.

Herein, we have calculated the NICS_{zz} values taken at the center of **A**, **B** and **C** rings (Figure 1) of **1–9** for z = -5 to +5 Å, in order to check their validity as aromaticity descriptors, compared to the NICS values obtained *via* xyz-scan. It is known^[23] that the magnetic properties of a molecule can detect





Figure 6. Magnetic anisotropy and NICS_{xz} values along the x axis (Figure 1) for 1–9 at MP2/6-311 + +G(d,p).

an (anti)aromatic π delocalization but are susceptible to σ -and π -triggered local anisotropies. π -Density anisotropy in 6-membered heterorings is known $^{[41,66-70]}$ to be rather insensitive

to the heteroatom(s). A direct link between π -density anisotropy and aromaticity has been proposed as a probe for heterocycles.^[71]





Figure 7. Magnetic anisotropy (Δ Anisotropy) and NICS_{xz} (Δ NICS_{xz}) values along the x axis (Figure 1) for 1–9 (solid lines) and for 2–9 with respect to 1 (dash lines) at MP2/6-311 + +G(d,p).

Table 3. Maximum NICS $_{xyz}$ values and magnetic anisotropy and for 1–9 at z distances above the plane of the molecule at MP2/6-311+ + G(d,p).								
Comp.	NICS _{xy}							
Z=	0.8	1.2	1.6	2.0	2.4			
1	-22.28	-12.68	-7.93	-5.43	-3.95			
2	-21.86	-12.06	-7.31	-5.02	-3.60			
3	-21.07	-10.78	-5.89	-3.88	-2.69			
4	-18.85	-9.92	-5.74	-3.83	-2.66			
5	-21.85	-11.19	-6.50	-4.37	-3.02			
6	-24.10	-12.91	-7.20	-4.65	-3.18			
7	-21.46	-11.37	-6.59	-4.50	-3.14			
8	-22.27	-11.75	-6.88	-4.76	-3.32			
9	-22.02	-11.69	-6.84	-4.60	-3.24			
	Anisotropy							
1	40.08	33.73	26.79	20.82	16.11			
2	36.33	30.69	24.40	18.98	14.75			
3	28.96	24.90	20.02	15.65	12.19			
4	28.87	24.41	19.65	15.15	11.75			
5	31.26	26.60	21.36	16.56	12.83			
6	31.38	26.96	22.45	17.23	13.09			
7	33.23	28.12	22.36	17.37	13.48			
8	34.50	29.06	23.02	17.82	13.79			
9	34.43	29.00	22.92	17.73	13.70			

Plots of NICS_{zz} and (an)isotropy values, along the z axis (Figure 1), are depicted in Figure 4 and Figurea S1-S4 of SI. Note that both methods predict almost the same plots. Values in plane (z=0), at $z = \pm 5$ Å (infinity) and at their extremes are given in Table 1 and Tables S1–S6 of SI. At ca. 5 Å all values converge implying that aromaticity is no longer of any significance. The A ring of the 2-9 series displays its highest antiaromaticity and magnetic anisotropy for z=0, i.e., on the ring's plane. The highest antiaromaticity (NICS₇₇=11.8) and highest magnetic anisotropy (31.0) is observed in 6, whereas the lowest antiaromaticity (6.9) and lowest magnetic anisotropy (23.4) is found in 2. The relative descending order of antiaromaticity of the series is 6 > 4,5,9 > 8 > 3,7 > 2. The B and C rings, on the other hand, display their highest anisotropy and aromaticity at ca. 1.2 Å and 0.8 Å, respectively, above the xy plane. From the $NICS_{zz}$ values (Table 1) one can see that the ${f C}$ ring demonstrates a higher aromatic character than its B partner with 5 and 6 reversing this order. The existence of the heteroatoms (or the CH₂ in 2) results in an increase of the aromaticity of the C ring in its center. Specifically, for the C ring, **2** and **7–9** present similar NICS_{zz} values (similar aromaticities) at about -10.6, while **3–6** at about -9.0. Thus, position X (X=CH₂ or O) results in a higher aromaticity of **C** than in **3–6**.

Using the naphthalene core, as the building block of 2-9, the relative $NICS_{zz}$ ($\Delta NICS_{zz}$) and magnetic anisotropies values were plotted against z, see Figure 5 and Figures S5-S6 of SI. Δ NICS_{zz} and magnetic anisotropy values reveal discernible variations among B and C rings. Most notable of them are observed at *ca*. z=0.3 Å. B rings appear to be less aromatic than C. Their C partners, however, exhibit variable aromaticity. Thus, higher aromaticity in 7–9, at distances up to z=0.7 Å (Tables S2 and S5 of SI) and lower aromaticity at 1.7 Å for 2 and 8, at 1.4 Å for 7 and 9 and at ca.1 Å for 3-6 is observed. The resulting magnetic anisotropy and aromaticity order for the series is $1 \ge 2 > 8,7,9 > 5,6 > 4,3$ and $1,8 > 2 > 7,9 \ge 4 > 6,5 > 3$, respectively. Data, so far, suggest that it is the heteroatom number (e.g. three Ns in 6 or N,O in 7-9) rather than their relative arrangement in the bridge (i.e., 1,2- and 1,3- isomers 4 and 5) that exerts an effect on their aromaticity.

NICS_{xz} along the x symmetry axis of naphthalene core: Plots of $NICS_{xz}$ and (an)isotropy values for the series, along the x symmetry axis of 1 (see Figure 1), ranging from x = -5 to 5 Å and at distances z=0 (in plane) to z=2.0 Å above it, are depicted in Figure 6 and Figures S7,S8 of SI. The x axis dissects the naphthalene \boldsymbol{B} and \boldsymbol{C} rings. The highest NICS_{xz} values are observed at z=0 (in the ring plane), specifically along the fusion $C_{6a}\text{-}C_{9aa}$ bond as well as the $C_4\text{-}C_5$ and $C_8\text{-}C_9$ bonds. 3displays the highest aromaticity (-44.5) and 1 the lowest one (-41.7) of the series. This finding suggests that the A ring "contributes" to an elevation of the aromaticity of 1. The latter and 3 have the highest and lowest maximum anisotropy, respectively, the former located at the fusion bond and those at its either side, as shown above and the latter at the center of the **B** and **C** rings. Using, again, the NICS_{xz} and magnetic anisotropy values with reference to 1, plots along the x axis are shown in Figures S9, S10 of SI. In this case, once again, the B ring demonstrates more variations than its C partner in 2, 7 and 8 while the reverse is observed in 5 and 6. Magnetic anisotropy is highest throughout the series at z=0.3 Å. The corresponding aromaticity is also highest in the C ring of the series. It is located around the bonds already mentioned earlier (see Figures S9 and S10 of SI) with higher values following an

Full Papers doi.org/10.1002/slct.202004237





Figure 8. xy Contour plots of NICS_{xy} values along the z axis for the 1–7 compounds at MP2/6-311 + + G(d,p). (Red lines correspond to the smallest values and blue lines corresponds to the largest values).



Figure 9. xy Contour plots of NICS_{xy} values along the z axis for the 8–9 compounds at MP2/6-311 + +G(d,p). (Red lines correspond to the smallest values and blue lines corresponds to the largest values)



Figure 10. NICS $_{xyz}$ values (the most negative values of xy planes) along the z axis for the 1–9 compounds at MP2/6-311 + +G(d,p).

increasing distance from the ring. At 2 Å (see Figure 7 and Figures S11, S12 of SI) aromaticity of **B** appears to precede that of the C ring in 7 and 8 whereas **C** ring takes the lead in 2,5 and 6. Eventually the overall order of aromaticity and anisotropy, along the x axis, are 3 > 8,7 > 5 > 4 > 9 > 6 > 2 > 1 and 1 > 2 > 8,9 > 7 > 5 > 6 > 4 > 3, respectively (see Table 2 and Table 9S of SI) and as z distance from the plane of the rings is increased, the variations of NICS_{xz} values, along the x axis, are diminished.

NICS_{xyz}: xy-scan contour plots of magnetic (an)isotropy and NICS values, along the z axis, are given in Figures 8 and 9 and Figures S13, S14 of SI, while their maximum values are shown in Figure 10, Table 3 and Tables S8 of SI. In both parameters, values are higher close to the plane and depressed moving

away from it (Figure 11 and Figure S15 of SI). 3 and 4 display the lowest and 1 the highest aromaticity values, with an ordering of the series as 6 > 1 > 8 > 9 > 2 > 5 > 7 > 3 > 4 at the lowest distance (z=0.8 Å), changing to 1 > 2 > 8 > 9 > 6 > 7 > 5 > 3 > 4 at the highest one (z=2.4 Å). On the other hand, magnetic anisotropy ordering remains virtually unchanged with increasing distance from the plane as 1 > 2 > 8 > 9 > 7 > 6 > 5 > 3 > 4 (see Figure 11 and Figure S16 of SI).

Comparison of NICS approaches and trends: Relative ordering of aromaticity and magnetic anisotropy of the series, along the various scans, at different z distances, are given in Table 4. Relative aromaticity varies with the heteroatom(s) of **A** ring and the z distance from the plane of the rings. Indicatively, **6** exhibits highest aromaticity at 0.8 Å and 1.2 Å, but it drops with increasing z distance, **3** has its highest aromaticity along the x symmetric axis of naphthalene core while it is depressed along the other scans. **1** appears to be the most aromatic of the series (in most scans), in agreement with earlier relevant reports on azanaphthalenes.^[41,62] Divergent aromaticity with obscure discrepancies has also been found in di- and triazines.^[24,70]

Comparing the aromaticity ordering obtained by NICS_{zz} and NICS_{xyz} indexes, we conclude that the use of the former at the center of the rings provides information only for local aromaticity, i.e., at the center of the rings. The NICS_{xyz} scan, however, appears to be the preferred one for a detailed description.

Magnetic anisotropy, on the other hand, remains almost unchanged in all z-, xz-, xy-, and xyz-scans. Higher values for **7**–**9** compared to **3**–**6** are found. On the contrary, (an)isotropic polarizability ordering predicts N–,N,N– and N,N,N–**3**–**6** members as more stable than their O–(and N,O–) doped congeners **7–9**.

Other published aromaticity indicators of 1-9,^[44] i.e., HOMA,^[72] I_{Ar} ,^[73] ABO,^[74] PDI,^[75] and FLU,^[76] along with the relative aromaticity ordering of 1-9, are given in SI, see Tables S13–S14.

Magnetic Anisotropy



2.0

2.4

Figure 11. Highest magnetic anisotropy values at xy planes along the z axis for the 1–9 compounds at MP2/6-311 + + G(d,p).

Z(Å)

1.6

1.2

0.8

Table 4. Relative descending ordering of the 1-9 compounds with respect to the aromaticity and the magnetic anisotropy along the z axes at the center of the rings, along the x symmetry axis of naphthalene, and on the xy planes lying on various z distances above the rings; and with respect to the dipole moment (µ), isotropic polarizability (ip), and anisotropic polarizability (ap) at MP2/6-311 + + G(d,p).

	Aromaticity									
	\mathbf{Z}_{B}	\mathbf{z}_{C}	х	ху	ху	ху	ху	ху	μ	
z=	0.8	0.8	0	0.8	1.2	1.6	2.0	2.4		
	1	1	3	6	6	1	1	1	8	
	9	8	8	1	1	2	2	2	5	
	6	2	7	8	2	6	8	8	6	
	5	7	5	9	8	8	6	9	3	
	2	9	4	2	9	9	9	6	9	
	8	4	9	5	7	7	7	7	7	
	7	6	6	7	5	5	5	5	2	
	4	5	2	3	3	3	3	3	4	
	3	3	1	4	4	4	4	4	1	
	Magı	Magnetic Anisotropy								ар
	1									
		1	1	1	1	1	1	1	3	3
	2	1 2	1 2	1 2	1 2	1 2	1 2	1 2	3 2	3 4
	2 9	1 2 8	1 2 8	1 2 8	1 2 8	1 2 8	1 2 8	1 2 8	3 2 4	3 4 5
	2 9 8	1 2 8 7	1 2 8 9	1 2 8 9	1 2 8 9	1 2 8 9	1 2 8 9	1 2 8 9	3 2 4 5	3 4 5 6
	2 9 8 6	1 2 8 7 9	1 2 8 9 7	1 2 8 9 7	1 2 8 9 7	1 2 8 9 6	1 2 8 9 7	1 2 8 9 7	3 2 4 5 7	3 4 5 6 2
	2 9 8 6 5	1 2 8 7 9 4	1 2 8 9 7 5	1 2 8 9 7 6	1 2 8 9 7 6	1 2 8 9 6 7	1 2 8 9 7 6	1 2 8 9 7 6	3 2 4 5 7 6	3 4 5 6 2 7
	2 9 8 6 5 7	1 2 8 7 9 4 5	1 2 9 7 5 6	1 2 8 9 7 6 5	1 2 9 7 6 5	1 2 9 6 7 5	1 2 9 7 6 5	1 2 8 9 7 6 5	3 2 4 5 7 6 8	3 4 5 6 2 7 8
	2 9 8 6 5 7 4	1 2 7 9 4 5 3	1 2 9 7 5 6 4	1 2 8 9 7 6 5 3	1 2 9 7 6 5 3	1 2 9 6 7 5 3	1 2 8 9 7 6 5 3	1 2 8 9 7 6 5 3	3 2 4 5 7 6 8 9	3 4 5 6 2 7 8 9

Of these HOMA, ABO and PDI predict 1 as the most aromatic compound, whereas I_A predicts 1 as the second aromatic compound and FLU as the compound with the least aromaticity! Furthermore, the relative ordering of the series is far from informative as scattering and discrepancies are abundant. This is hardly surprising when handling polyheterocycles. Interestingly, PDI, calculated for each ring separately, predicts similar to the NICS values on the xy plane along z axis at 2.0–2.4 Å, i.e., 1 > 2 > 9 > 7 > 8 > 5 > 6 > 3 > 4 (PDI) and 1 > 2 > 8 > 9 > 6 > 7 >5>3>4 (NICS). Generally, aromaticity cannot be sufficiently described by looking at each ring separately (e.g., using HOMA, FLU, PDI, I_A , ABO) given that π electron density is spread over the entire structure. We believe that it is the whole space around the compounds that gives the best description not a mean value. It is known^[52] that of the available methods, NICSxyz-scan and current density analysis are suited best for this type of structures.

Chemistry Europe

European Chemical Societies Publishing

Clearly, in the present series (a) aromaticity and anisotropy vary according to the nature of the heteroring (heteroatom (s) size, electronegativity and relative position) as well as the position of their measurement with respect to the plane of the structures and (b) the contribution of the σ component to the total density dominates close to the ring plane while the π component picks up in significance with increasing distance from the plane. Thus, the ring heteroatom(s)- triggered π perturbation (mainly an outcome of N,N and N,O lone pair repulsions), has an insignificant effect on the anisotropy of σ skeleton. Indeed, an undirected π density anisotropy with a circular symmetry at RCPs in aromatics and a directed π density anisotropy with elliptic shape in antiaromatics are known.^[77]

Conclusions

In the present work, we study theoretically the effect of perifusion on naphthalene derivatives by the NICS-xyz scan. We conclude that:

- Relative aromaticity of the series 2–9 varies with respect to i) heteroatom nature of A ring, and ii) the distance from the plane of the ring.
- 1 shows the highest aromaticity at the center of B and C rings, followed by 8 (an O,N- derivative) at the C ring. For the series aromaticity is highest at the center of these rings, about 0.8 Å from the xy plane of the rings.
- Highest aromaticity is observed in the fusion C_{6a}-C_{9aa} bond, as well as the C_4 - C_5 and C_8 - C_9 bonds.
- Highest anisotropy values are observed in the naphthalene core bonds mentioned above while lowest values are found at the center of **B** and **C** rings.
- The relative aromaticity ordering of the series along: i) z axis, at the center of the rings, is $1,\!8\!>\!2\!>\!7,\!9\!\gg\!4\!>\!6,\!5\!>\!3,$ ii) xsymmetry axis of naphthalene, is 3 > 8,7 > 5 > 4 > 9 > 6 > 2 >1 and iii) z axis, on the xy plane, varies with z distance, i.e., 6>1>8>9>2>5>7>3>4 at Z=0.8 Å, changing to 1> 2>8>9>6>7>5>3>4 at 2.4 Å.
- The relative magnetic anisotropy ordering of the series remains virtually unchanged in all different approaches (z-, xz- xy- and xyz-scan), i.e., 1 > 2 > 8 > 9 > 7 > 6 > 5 > 3 > 4, similar to that for aromaticity at z = 2.4 Å.
- The N- (N,N- and N,N,N-) structures, i.e., 3-6, appear to be somewhat more stable than their O-(and N,O-) doped congeners, i.e., 7-9.

Peri-fusion of ring A increases the aromaticity of the structures along the x symmetry axis of naphthalene. In other words, it does, indeed, participate in the entire structure with



both its σ and π components as a heteroring not as a heterobridge.

Supporting Information Summary

Geometries, dipole moments, dipole electric field isotropic and anisotropic polarizability, magnetic isotropy and anisotropy contour plots and NICS indices and NICS-scan plots at B3LYP and MP2/6-311 + +G(d,p) level of theory are provided.

Acknowledgement

DT acknowledges Special Accounts for Research Grants for supporting this work by the project "SONFM" (KE 17034).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Aromaticity · Calculations · Naphthalene · NICS · N,N–, N,O-heterocyles.

- [1] a) S. Radenković, J. Kojić, J. Petronijević, M. Antić, J. Phys. Chem. A 2014, 118, 11591–11601; b) T. J. Ritchie, S. J. F. Macdonald, J. Med. Chem. 2014, 57, 17, 7206–7215.
- [2] a) T. M. Krygowski, H. Szatylowicz, O. A. Stasyuk, J. Dominikowska, Marcin Palusiak, Chem. Rev. 2014, 114, 6383–6422; b) S. Fias, S. Van Damme, P. Bultinck, J. Comput. Chem. 2010, 31, 2286–2293; c) S. Fias, P. W. Fowler, J. L. Delgado, U. Hahn, P. Bultinck, Chem. A Eur. J. 2008, 14, 3093–3099; d) M. K. Cyrański, B. T. Stępień, T. M. Krygowski, Tetrahedron 2000, 56, 9663–9667.
- [3] a) "Polycyclic Arenes and Heteroarenes: Synthesis, Properties, and Applications", Qian Miao ed., 2016, Wiley-VCH, Verlag GmbH & Co KGaA, Boschstr. 12, 69469 Weinheim, Germany; b) "Quantum Research on the Aromaticity of the Polycyclic Aromatic Hydrocarbons", Q. Han, J. Zhao, Z. Jiang, H. Wen, *Energy Environ. Focus* 2015, 4(2), 145–148; c) J. Durdević, I. Gutman, J. Terzić, A. T. Balaban, *Polycyclic Aromat. Compd.* 2009, *29*, 90–102.
- [4] a) A. Ciesielski, T. M. Krygowski, M. K. Cyrański, J. Chem. Inf. Model. 2008, 48, 1358–1366; b) J. Poater, R. Visser, M. Sola, F. M. Bickelhaupt, J. Org. Chem. 2007, 72, 1134–1142.
- [5] A. T. Balaban, D. C. Oniciu, A. R. Katritzky, Chem. Rev. 2004, 104, 2777– 2812.
- [6] A. T. Balaban, Top. Heterocycl. Chem. 2009, 19, 203-, T. M.Krygowski, M. Cyrański, vol. eds., Springer.
- [7] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* 2005, 105, 3842–3888.
- [8] a) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* 2012, *41*, 7857–7889 and references cited therein; b) B. T. Haire, K. W. J. Heard, M. S. Little, A. V. S. Parry, J. Raftery, P. Quayle, S. G. Yeats, *Chem. Eur. J.* 2015, *21*, 9970–9974.
- [9] a) J. E. Anthony, Angew. Chem. Int. Ed. 2008, 47, 452–483; Angew. Chem.
 2008, 120, 460–492; b) H. Alyar, Rev. Adv.Mater. Sci. 2013, 34, 79–87 and references cited therein.
- [10] a) E. Mondal, W.-Y. Hung, H.-C. Dai, K.-T. Wong, Adv. Funct. Mater. 2013, 23, 3096–3105; b) W.-Y. Hung, G.-C. Fang, S.-W. Lin, S.-H. Cheng, T.-Y. Kuo, K.-T. Wong, P.-T. Chou, Sci. Rep. 2014, 4, 5161–5165.
- [11] a) R. A. Kanaly, Sh. Harayama, Microbiol. Biotechnol. 2010, 3, 136–164.
- [12] T. M. Krygowski, J. Chem. Inf. Comput. Sci. 1993, 33, 70–78.
- [13] M. K. Cyrański, Chem. Rev. 2005, 105, 3773–3811.
- [14] M. Homray, A. Misra, P. K. Chattaraj, Curr. Org. Chem. 2017, 21, doi: 10.2174/1385272821666170428124343.
- [15] R. Gershoni-Poranne, A. Stanger, Chem. Soc. Rev. 2015, 44, 6597-6615.
- [16] J. Poater, M. Duran, M. Sola, B. Silvi, *Chem. Rev.* 2005, *105*, 3911–3947.
 [17] A. Ciesielski, T. M. Krygowski, M. K. Cyrański, M. A. Dobrowolski, A. T. Balaban, *J. Chem. Inf. Model.* 2009, *49*, 369–376.

- [18] F. Feixas, E. Matito, J. Poater, M. Sola, Chem. Soc. Rev. 2015, 44, 6434– 6451.
- [19] K. Cocq, C. Lepetit, V. Maraval, R. Chauvin, Chem. Soc. Rev. 2015, 44, 6535–6559.
- [20] H. Szatylowicz, O. A. Stasyuk, T. M. Krygowski, Adv. Heterocycl. Chem. 2016, 120, 301–327.
- [21] I. Fernandez, G. Frenking, G. Merino, Chem. Soc. Rev. 2015, 44, 6452–6463.
- [22] S. Paul, T. Goswami, A. Misra, AIP Adv. 2015, 5, 107211.
- [23] D. Setiawan, E. Kraka, D. Cremer, J. Org. Chem. 2016, 81, 9669–9686.
- [24] M. Solà, F. Feixas, J. O. C. Jiménez-Halla, E. Matito, J. Poater, Symmetry 2010, 2, 1156–1179.
- [25] P. Lazzeretti, Phys. Chem. Chem. Phys. 2004, 6, 217–223.
- [26] G. Portella, J. Poater, M. Solà, J. Phys. Org. Chem. 2005, 18, 785-791.
- [27] V. V. Mezheritskii, V. V. Tkachenko , Adv. Heterocycl. Chem. 1990, 51, 1– 103.
- [28] a) R. A. Kanaly, Sh. Harayama, *Microbiol. Biotechnol.* 2010, *3*, 136–164;
 b) N. R. Candeias, L. C. Branco, P. M. Gois, C. A. Alfonso, A. F. Trindale, *Chem. Rev.* 2009, *109*, 2703–2802.
- [29] a) N. P. Tsvetkov, E. Gonzalez-Rodriguez, A. Hughes, G. dos Passos Gomes, F. D. White, F. Kuriakose, I. V. Alabugin, *Angew. Chem. Int. Ed.* 2018, *57*, 3651–3655; *Angew. Chem.* 2018, *130*, 3713–3717; b) S. Sarkar, T. N. G. Row, *IUCrJ* 2017. *4*, 37–49; c) I. Majerz, T. Dziembowska, *J. Phys. Chem. A* 2014, *118*, 7118–7129.
- [30] R. A. Pascal, Chem. Rev. 2006, 106, 4809–4819.
- [31] M. Ball, Y. Zhong, Y. Wu, C. Schenck, F. Ng, M. Steigerwald, S. Xiao, C. Nuckolls, Acc. Chem. Res. 2015, 48, 267–276.
- [32] C.-N. Feng, Y.-C. Hsieh, Y.-T. Wu, Chem. Rec. 2015, 15, 266–279.
- [33] a) H. Shadnia, J. S. Wright, J. Chem. Theory Comput. 2009, 5, 1129–1136;
 b) R. Peck, J. M. Schulman, R. L. Disch, J. Phys. Chem. 1990, 94, 6637–6641.
- [34] K. B. Wiberg, Angew. Chem. Int. Ed. Engl. 1986, 25, 312-322.
- [35] G. J. Bodwell, J. N. Bridson, T. J. Houghton, J. W. J. Kennedy, M. R. Mannion, Angew. Chem. Int. Ed. 1996, 35, 1320–1321; Angew. Chem. 1996, 108, 1418–1420.
- [36] V. Aksenov, A. S. Lyakhovnenko, N. A. Aksenov, I. V. Aksenova Rev. J. Chem. 2012, 2, 208–239.
- [37] C. Gil, S. Bräse, J. Comb. Chem. 2009, 11, 176–197.
- [38] A. Gomtsyan, Chem. Heterocycl. Compd. 2012, 48, 7–10.
- [39] a) J. Dominikowska, M. Palusiak, Struct. Chem. 2012, 23, 1173–1183;
 b) M. Andrzejak, P. Kubisiak, K. K. Zborowski, Struct. Chem. 2013, 24, 1171–1184;
 c) B. Hou, P. Yi, Z. Wang, S. Zhang, J. Zhao, R. L. Mancera, Y. Cheng, Z. Zuo, Comput. Theoret. Chem. 2014, 1046, 20–24;
 d) J. I. Wu, J. E. Jackson, P.v.R. Schleyer, J. Am. Chem. Soc. 2014, 136, 13526–13529.
- [40] a) M. Buhl, C. Von Wullen, *Chem. Phys. Lett.* **1995**, *247*, 63–68; b) P. von Rague Schleyer, J. I. Wu, F. P. Cossio, I. Fernandez, *Chem. Soc. Rev.* **2014**, *43*, 4909–4921 and references cited therein.
- [41] Y. Wang, J. I.-C. Wu, Q. Li, P. von Rague Schleyer, Org. Lett. 2010, 12, 4824–4827.
- [42] a) M. Sola, Front. Chem. Theoret. Comput.Chem. 2013, 1, 1–8; b) R. Kalescky, E. Kraka, D. Cremer, J. Phys. Chem. 2014, 118, 1948–1963; c) F. Mao, W. Ni, X. Xu, H. Wang, J. Wang, M. Ji, J. Li, Molecules 2016, 21, 75–93; d) S. K. Pandey, D. Manogaran, S. Manogaran, H. F. Schaefer III, J. Phys. Chem. A 2016, 120, 2894–2901; e) M. Antic, B. Furtula, S. Radenkovic, J. Phys. Chem. A 2017, 121, 3616–3626.
- [43] C. A. Ramsden, Tetrahedron 2010, 66, 2695–2699.
- [44] D. Tzeli, P. Kozielevicz, M. Zloh, D. Antonow, P.G. Tsoungas, I.D. Petsalakis, *ChemistrySelect* 2018, 3, 9743–9752.
- [45] a) D. Becke, J. Chem. Phys. 1993, 98, 1372–1377; b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B. 1988, 37, 785–789.
- [46] M. J. Frisch, M. Head-Gordon, J. A. Pople, "Direct MP2 gradient method," Chem. Phys. Lett. 1990, 166, 275–80.
- [47] L. A. Curtiss, M. P. McGrath, J.-P. Blandeau, N. E. Davis, R. C. Binning Jr, L. Radom J. Chem. Phys. **1995**, 103, 6104–6113.
- [48] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, J. Am. Chem. Soc. 1996, 118, 6317–6318.
- [49] U. Fleischer, W. Kutzelnigg, P. Lazzareti, V. Mühlenkamp, J. Am. Chem. Soc. 1994, 116, 5298–5306.
- [50] J. O. C. Jiménez-Halla, E. Matito, J. Robles, M. Sola, J. Organomet. Chem. 2006, 691, 4359–4366.
- [51] A. Stanger, J. Org. Chem. 2006, 71, 883–893.



- [52] a) R. Gershoni-Poranne, A. Stanger, *Chem. Eur. J.* 2014, *20*, 5673–5688;
 b) R. Gershoni-Poranne, *Chem. Eur. J.* 2018, *24*, 4165–4172.
- [53] a) F. London J. Phys. Radium 1937, 8, 397–409. b) J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, J. Chem. Phys. 1996, 104, 5497–509.
- [54] 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. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. A.Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, Gaussian 16, Revision C.01.
- [55] S. Hashimoto, S. Nakatsuka, M. Nakamura, T. Hatakeyama, Angew. Chem. Int. Ed. 2014, 53, 14074–14076; Angew. Chem. 2014, 126, 14298–14300.
- [56] a) D. Tzeli, P. G. Tsoungas, I. D. Petsalakis, P. Kocielewicz, M. Zloh, *Tetrahedron* 2015, 71, 359–369; b) P. Supsana, P. G. Tsoungas, A. Aubry,
 S. Skoulika, G. Varvounis, *Tetrahedron* 2001, 57, 3445–3453; c) P. Supsana, P. G. Tsoungas, G. Varvounis, *Tetrahedron Lett.* 2000, 41, 1845–1848.
- [57] C. Foroutan-Nejad, S. Shahbazian, P. Rashidi-Ranjbar, Phys. Chem. Chem. Phys. 2010, 12, 12630–12637; Phys. Chem. Chem. Phys. 2011, 13, 12655– 12658.
- [58] C. Foroutan-Nejad, Z. Badri, S. Shahbazian, P. Rashidi-Ranjbar J. Phys. Chem. A 2011, 115, 12708–12714.
- [59] C. Foroutan-Nejad, S. Shahbazian, F. Feixas, P. Rashidi-Ranjbar, M. Solà, J. Comput. Chem. 2011, 32, 2422–2431.

- [60] C. Foroutan-Nejad, J. Vicha, A. S. Ghosh, Phys. Chem. Chem. Phys. 2020, 22, 10863–10869.
- [61] P. Lazzeretti, Prog. Nucl. Magn. Reson. Spectrosc. 2000, 36,1-88.
- [62] a) M. V. Zhigalko, O. V. Shishkin, J. Struct. Chem. 2006, 47, 823–830; b) L.
 Wang, H. Wang, Intern. J. Quant. Chem. 2007, 107, 1846–1855.
- [63] Polarizability determines the dynamic response of a molecule to an external field, thus, providing an insight into the molecule's structure.[64] M. Baranac-Stojanović, *RSC Adv.* 2014, *4*, 308–321.
- [65] R. J. Doerksen, V. J. Steeves, A. J. Thakkar, J. Comput. Methods Sci. Eng. 2004, 4, 427–438.
- [66] V. Omelchenko, O. V. Shishkin, L. Gorb, J. Leszczynski, S. Fias, P. Bultinck, Phys. Chem. Chem. Phys. 2011, 13, 20536–20548.
- [67] E. R. Ghiasi, C. Foroutan-Nejad, THEOCHEM 2010, 941, 47–52.
- [68] J. I. Wu, F. G. Puhlhofer, P. v. R. Schleyer, R. Puchta, B. Kiran, M. Mauksch, N. J. R. v. E. Hommes, I. Alkorta, J. Elguero, J. Phys. Chem. A 2009, 113, 6789–6794.
- [69] D. Sulzer, M. Olejniczak, R. Bast, T. Saue, Phys. Chem. Chem. Phys. 2011, 13, 20682–20689.
- [70] E. D. Raczyńska, M. Hallman, K. Kolczyńska, T. M. Stepniéwski, Symmetry 2010, 1485–1509.
- [71] R. Firouzi, S. Sh. Ardani, Phys. Chem. Chem. Phys. 2014, 16, 11538–11548.
- [72] F. De Proft, P. Geerlings, Chem. Rev. 2001, 101 1451-1464.
- [73] C. W. Bird, Tetrahedron **1996**, 52, 9945–9952.
- [74] E. Matito, P. Salvador, M. Duran, M. Solà, J. Phys. Chem. 2006, 110, 5108– 5113.
- [75] J. Poater, X. Fradera, M. Duran, M. Solà, Chem. Eur. J. 2003, 9, 400-406.
- [76] E. Matito, M. Duran, M. Solà, J. Chem. Phys. 2005, 122, 014109.
- [77] R. Firouzi, Chem. Phys. Lett. 2014, 595–596, 48–54.

Submitted: November 6, 2020 Accepted: January 22, 2021