DFT exploration of structural and magnetic properties of [n]annulene ring carbomers

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DFT calculations of structural and magnetic properties of the ring carbomers of [n]annulenic species (n = 3–6), show that the aromatic *vs.* antiaromatic character of [n]annulenic species is qualitatively preserved by the carbomerisation process.

The constitutive, practical, and aesthetical importance of the carbon element in molecular chemistry[1] can be doubled with a formal function to expand the size of Dreiding (or ball-and-stick) models of molecules independently from other structural features. Indeed, by inserting an (sp-C)$_2$ unit into each bond of a Lewis structure, one constructs a so-called 'carbomer' structure of the former which has approximately a three-fold expanded size, and yet preserves the connectivity, the symmetry, the shape and π-electron resonance properties of its antecedent (Scheme 1).[2]

X—Y ⇨ X—C≡C—Y   X=Y ⇨ X=C=C=Y   X≡Y ⇨ X≡C—C≡Y
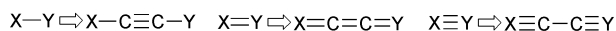
**Scheme 1** Basic process in the definition of carbomers.

The general question to be addressed is whether the preservation/transformation of such essential characteristics of the chemical model entails preservation/transposition of physicochemical properties. The addition of two π-electron pairs per connection in the carbomerisation process makes a carbomer molecule *a priori* more reactive than the parent molecule. In order to correct this additive bond energy scheme and restore some stability in future synthetic targets, one here considers possible aromatic carbomer molecules: these molecules might simply be the carbomers of known aromatic molecules. This would allow us to test the way aromaticity, an intensively long debated concept,[3] is transposed by the carbomerisation process. In an exploratory study, we now consider the 'ring carbomers' of [n]annulenic species.[4]

Lewis structures of the ring carbomers **nb** of the lowest classical [n]annulenic molecules and ions **na** (n = 3–6) are depicted in Scheme 2.[5] According to the simple VSEPR model, the structures should be planar and more or less symmetrical,

depending on the electron delocalisation. Although none of these molecules are experimentally known,[6] substituted derivatives of the ring carbomer of benzene **6b** have been described.[7] In particular, the D_{6h} symmetry of the ring of the hexaphenyl derivative has been established by X-ray crystallography.[8] Since geometry optimisation of **6b** at the B3PW91/6-31G** level reproduced the experimental symmetry and bond lengths, this method was used for calculating the structures of all carbomers **nb** (Fig. 1).

As anticipated from the application of the basic Hückel rule to the sole π$_z$-electron systems,[9] the singlet $4m + 2$ π$_z$ electron structures **nb** (n = 6, 5, 3) and the triplet $4m$ π$_z$-electron structure **nbT** (n = 4), exhibit D_{nh} symmetry just as their respective parent molecules **na**. Likewise, the singlet $4m$ = 12 π$_z$-electron structure **4bS** possesses a lower D_{2h} symmetry just as its parent singlet cyclopentadiene **4aS** (Table 1). These results prove that structural aromaticity (resp. structural anti-aromaticity) of a [n]annulenic species **na** is preserved in its ring carbomer **nb**. Moreover, the application of the Hückel rule, early established for [n]annulenic molecules, is thus valid for their ring carbomers on the basis of a π$_z$ electron count. The specific presence of in-plane π$_{xy}$ electrons does not have a qualitative influence on the structural aromaticity of [n]annulene ring carbomers.

According to Katritsky's factor analysis, the aromaticity concept is two dimensional.[10] Whereas structural aromaticity (D_{nh} symmetry) can be regarded as a measure of the cyclic delocalisation of σ electrons,[11] magnetic aromaticity (ring current) is a measure of the cyclic delocalisation of the π electrons.[12] The Nucleus Independent Chemical Shift (NICS), propounded by Schleyer in 1996, proves to be a universal magnetic aromaticity measure revealing the existence of an overall diatropic ring current when negative, and an overall paratropic ring current when positive.[13] The NICS values of the optimised structures **nb** (n = 3–6) have been calculated at the ring center, at the B3LYP/6-31+G* level within the framework of GIAO formalism.[14] The data are compared with the NICS values of corresponding [n]annulenic species (Table 1):[15] ring
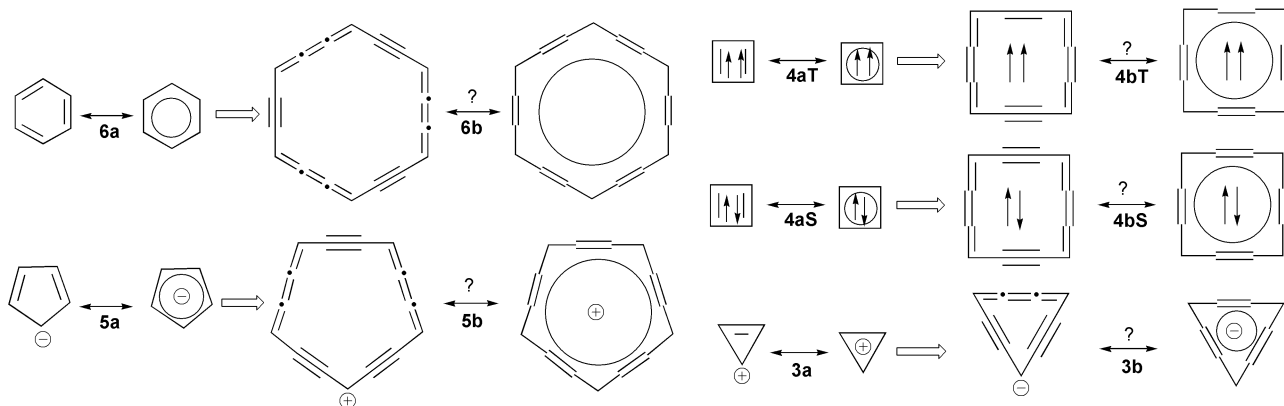

Scheme 2 [n]annulenic species and their ring carbomers.

Table 1 Comparative DFT-computed structural and magnetic data of [*n*]annulenic structures *na* and their ring carbomers *nb*

No	Geometry[a]	sp–sp	sp–sp²	sp–sp²–sp	sp²–sp–sp	NICS[b]	No	Geometry[a]	sp²–sp²	NICS[b]
6b	D_{6h}	1.239	1.369	122.6°	178.7°	−17.9	**6a**	D_{6h}	1.394	−8.0
5b	D_{5h}	1.238	1.369	118.5°	174.8°	−16.9	**5a**	D_{5h}	1.419	−12.5
4bT	D_{4h}	1.241	1.378	115.2°	167.4°	−15.8	**4aT**	D_{4h}	1.437	−2.0
4bS	D_{2h}	1.267,1.218	1.334, 1.428	115.2°	167.3°	53.0	**4aS**	D_{2h}	1.572, 1.334	28.2
3b	D_{3h}	1,253	1.391	109.7°	155.1°	−22.3	**3a**	D_{3h}	1.365	−22.4

[a] Optimised geometries at the B3PW91/6-31G** level. Bond lengths are in Å units. [b] In ppm units. NICS were calculated at the centroids of the rings within the framework of the GIAO formalism at the B3LYP/6-31+G* level from the B3PW91/6-31G** optimised geometries.
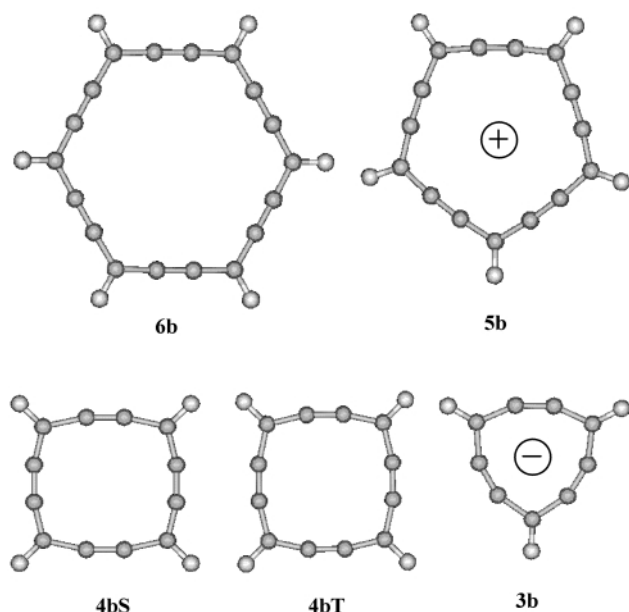
Fig. 1 Optimised geometries of ring carbomers *nb* at the B3PW91-6-31G** level.

carbomers *nb* have the same NICS sign as their respective parent [*n*]annulenes *na*. This shows that magnetic aromaticity is qualitatively preserved in the carbomerisation process. The high positive NICS value of singlet 12-π_z electron **4bS** must be emphasised: it is the signature of a rather strong paratropic ring current, as in singlet cyclobutadiene.

In order to bring out the specific influence of the out-of-plane π_z system *versus* that of the in-plane π_{xy} system in the ring carbomer structures *nb*, the π_{xy} in-plane system is formally isolated in the corresponding [*n*]pericyclynes. For example, the ring center NICS value of [5]pericyclyne **7** (Scheme 3) in its optimised geometry has been calculated. The weak value found (NICS(**7**) = +0.6 ppm, at the HF/6-31+G* level) confirms the absence of homoaromaticity in **7** claimed by Schleyer *et al.*[16] The ring geometry of **7** is D_{5h} (with $d(C\equiv C)$ = 1.208 and $d(C-C)$ = 1.466 Å), similar to that of **5b**. Therefore, by
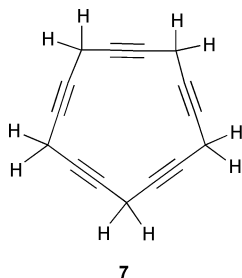
Scheme 3 [5]pericyclyne, assumed to have a π_{xy} system similar to that of **5b**.

resorting to the additive scheme NICS ≈ NICS(σ) + NICS(π_z) + NICS(π_{xy}),[17] it can be approximated that **7** and **5b** have similar NICS(σ) and NICS(π_{xy}) contributions: the high NICS value of **5b** is thus merely due to the NICS(π_z) component, while the in-plane π_{xy} system plays a minor role.

As for [*n*]annulenes, structural and magnetic aromaticity criteria correlate perfectly well together and with the Hückel rule applied to the sole π_z-electron system of [*n*]annulene ring carbomers. In conclusion, the preservation of aromaticity *vs.* antiaromaticity character during the carbomerisation process is clearly illustrated. This result encourages further efforts in the carbomeric comparison of physicochemical properties. In particular the transposition of energetic aromatic criteria going from *na* to *nb* will be reported shortly.[18]

Notes and references

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4 Since substituents generally exert a weak influence on the aromaticity of the benzene ring, peripheral C–H bonds are not required to undergo C_2-insertion. Therefore, in a preliminary study, the VSEPR symmetry of the Dreiding structures is preserved, but not the exact shape.
5 In order to satisfy the Hückel rule for **5b** and **6b**, one decides to define the carbomer of a charged species as the everywhere C_2-inserted structure with an opposite whole charge. In the case of non-covalent neutral structures, this is formally equivalent to a reversal of the charge separation.
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