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Paramagnetic ring current effects in anti-aromatic structures subject to substitution/annelation quantified by spatial magnetic properties (TSNMRS)

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ABSTRACT

The spatial magnetic properties, through-space NMR shieldings (TSNMRS), of the typically anti-aromatic cyclopentadienyl cation, cyclobutadiene, pentalene, *s*-indacene and of substituted/annelated analogues of the latter structures have been calculated using the GIAO perturbation method employing the nucleus independent chemical shift (NICS) concept and visualized as iso-chemical-shielding surfaces (ICSS) of various size and direction. The TSNMRS values were employed to visualize and quantify the dia(para) magnetic ring current effects in the studied compounds. The interplay of dia(para)magnetic ring current effects due to substitution/annelation caused by heavy *exo*-cyclic *n*,*π*-electron delocalization can be qualified.

1. Introduction

While cyclic $(4n+2)$ π-electron conjugation leads to additional stabilization of *aromatic* compounds, cyclic conjugation of only 4*n* π-electrons results in destabilization of the corresponding, so-called *anti-aromatic* compounds. The theory behind *anti-aromaticity* has been developed by Breslow and coworkers[1] and refined in a number of recent papers.[2] Fundamental criteria[3] for anti-aromatic structures are of geometric (*bond length alternation* – Krygowski's HOMA index),[4] of energetic (*π-electronic energy* of the cyclic conjugated system higher than a non-cyclically delocalized reference system) and of magnetic origin (^{1}H NMR spectroscopic Δδ/ppm and Schleyer's NICS index).[5]

Highly conjugated aromatic/anti-aromatic compounds are more and more interesting for the opto-electronic industry as new organic functional material.[6] Herby, in order to quantify structural requirements for useful organic semiconductors, the knowledge about degree and scale of π-electron delocalization, the interplay of aromaticity/anti-aromaticity and their mutual influence are general internal preconditions. For these reasons we employed our TSNMRS concept[7] to qualify anti-aromatic species subject to substitution and annulation, respectively. Along this concept,[7] the spatial magnetic properties (through-space NMR shieldings – TSNMRS) are calculated for a grid surrounding the molecules in order to locate diatropic and paratropic regions of the molecules studied; the TSNMRS are visualized as iso-chemical-shielding surfaces (ICSS) and employed to visualize, qualify and quantify anisotropic effects of functional groups and dia(para)magnetic ring current effects of aromatic/anti-aromatic molecular structures.[7] While normally employed specifications of spatial magnetic properties to quantify (anti)aromaticity are theoretical items, experimental Δδ/ppm in proton NMR spectra are the molecular response property of TSNMRS values.[8]

To study substituent influences, the anti-aromatic cyclopentadienyl cation **1** was 3,4-NMe_2 disubstituted **2**, 2,5-NMe_2- (**3**) and 2,5(=CH–NMe_2)-disubstituted (**4**) (cf. Scheme 1). The dimethyl-amino group proves to be one of the strongest +M substituents – heavy *exo*-cyclic *n*,*π*-conjugation can be expected and will hereby influence the size of the present *4π* anti-aromaticity of the cyclopentadienyl moiety. The appropriate effect of *mono-* and *dis*-annelation on 4π-, 8π- and 12π-*anti*-aromaticity in **5a,b, 6a,b to 7a–d**, respectively, was tested employing the

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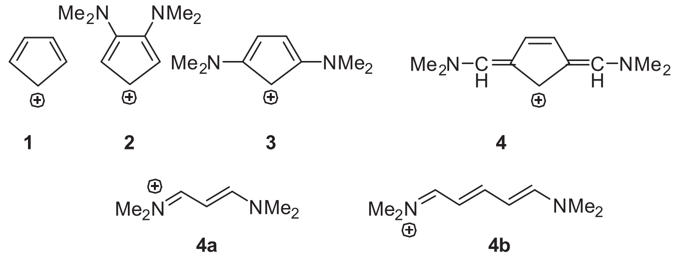


Scheme 1. Compounds studied.

corresponding fundamental anti-aromatic molecules cyclobutadiene (**5**), pentalene (**6**) and *s*-indacene (**7**) (cf. Scheme 2). These are the topics of the present study.

2. Computational details

The quantum chemical calculations were performed using the Gaussian 09 program package[9] and carried out on LINUX clusters. The studied structures were fully optimized at the MP2/6-311G(*d*,*p*) level of theory without constraints.[10] The obtained structures have been confirmed as local minima by performing harmonic frequency calculations at the optimized geometries.[11]

NICS values[5] were computed on the basis of the MP2/6-311G(*d*,*p*) geometries using the gauge-including atomic orbital (GIAO) method[12,13] at the B3LYP/6-311G(*d*,*p*)[14] theory level[15]; variation of the basis set was found to be of non-significant influence on the NICS values. To calculate the spatial NICS, ghost atoms were placed on a lattice of −10 Å to +10 Å with a step size of 0.5 Å in the three directions of the Cartesian coordinate system. The zero points of the coordinate system were positioned at the centers of the studied structures. The resulting 68,921 NICS values, thus obtained, were analyzed and visualized by the SYBYL 7.3 molecular modeling software[16]; different iso-chemical-shielding surfaces (ICSS) of −0.1 ppm (red) deshielding, and 5 ppm (blue), 2 ppm (cyan), 1 ppm (greenblue) 0.5 ppm (green) and 0.1 ppm (yellow) shielding were used to visualize the TSNMRS of studied structures in the various figures. ICSS are a quantitative indication of the diamagnetic(paramagnetic) ring current effect in ^{1}H NMR spectroscopy[7]; the computed shielding(deshielding) ICSS qualify and quantify the corresponding ring current effect in ^{1}H NMR spectroscopy subject to distance from the molecular centre of the molecule (in Å).[7]

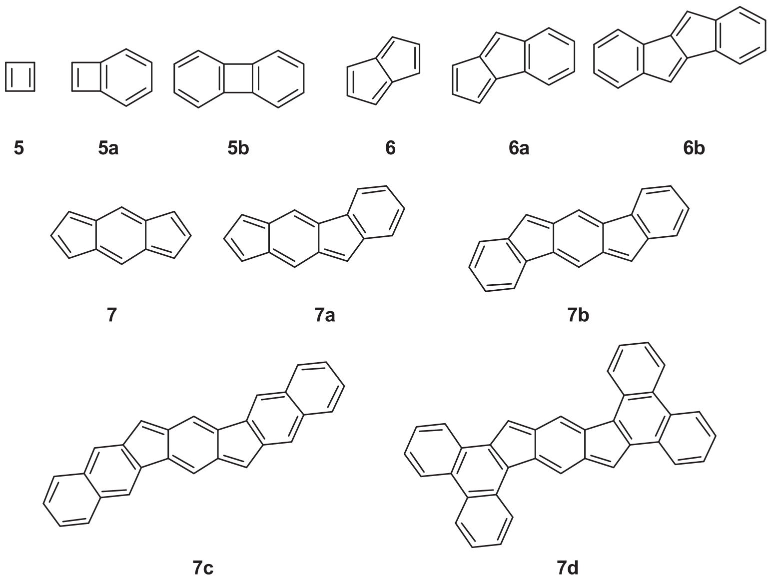
TSNMRS were computed and appropriately examined herein as the central topic of this paper. Of significant note though, there have been some later developments of the NICS index[17] showing that it is not the average NICS index as a single value, but rather the NICS(1)$_{zz}$ component only that need to be used to rigorously quantify aromaticity[18] and single average NICS values have even been proven to be unsuitable generally for the quantitative evaluation of aromaticity.[19] On the other hand, Stanger's NICS-XY scan[20] proved very successful in this respect.

3. Results and discussion

3.1. Structures of studied compounds

Influence of substitution on 4π-anti-aromaticity of cyclopentadienyl cation. As already mentioned along the *Introduction* the *energy criterion* is readily applicable only to typical mono-cyclic anti-aromatic systems (like cyclopentadienyl cation **1**) but not to molecules of more complex geometry and topology. Even if in the dimethylamino-substituted cyclopentadienyl cations **2** and **3** *exo*-cyclic n,π-conjugation is competing with 4π-*anti*-aromaticity of the central ring, they should have no anti-aromatic character due to the energy criterion.[21] In addition, present anti-aromatic character of the central 5-membered ring in **4** was assigned[21] although the pentamethine cyanine substructure in **4** was found (on the same *energy criterion*) to be the dominating, property-determining structure of the molecule. To get an idea of the effectivity of *n*,*π*-conjugation and still remaining 4π-*anti*-aromaticity in **1** − **4**, both the *geometric* and the *magnetic criterion* were computed and employed additionally.

The cyclopentadienyl cation **1** is a highly, thermally instable species and could not be isolated yet; except it is stabilized by a number of strongly electron-donating substituents[22] or stabilized as cobalt complex[23]; structural data concerning **2** to **4** are not available as well. The reported X-ray structure of pentamethylcyclopentadienyl cation[24] was actually the one of



Scheme 2. Compounds studied.