Nucleus-independent chemical shift criterion for aromaticity in π-extended tetraoxa[8]circulenes

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Abstract Recently synthesized π-extended symmetrical tetraoxa[8]circulenes that exhibit electroluminescent properties were calculated at the density functional theory (DFT) level using the quantum theory of atoms in molecules (QTAIM) approach to electron density distribution analysis. Nucleus-independent chemical shift (NICS) indices were used to characterize the aromaticity of the studied molecules. The tetraoxa[8] circulene molecules were found to consist of two antiaromatic perimeters (according to the Hückel "$4n$" antiaromaticity rule) that include 8 and 24 π-electrons. Conversely, NICS calculations demonstrated the existence of a common π-extended system (distributed like a flat ribbon) in the studied tetraoxa[8] circulene molecules. Thus, these symmetrical tetraoxa[8]circulene molecules provide examples of diatropic systems characterized by the presence of induced diatropic ring currents.

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Introduction

The synthesis and properties of tetraoxa[8]circulenes have attracted significant attention in the past decade [1–5]. Tetraoxa[8]circulenes are highly stable compounds that feature a central eight-membered ring surrounded by four benzene rings and four furan rings in an alternating manner. Both tetraoxa[8]circulenes and other heteroatom-substituted [8]circulenes (e.g., octathia[8]circulene and tetrathiatetraselena[8] circulene) [6, 7] have recently been used with great success in the construction of various devices used in materials science such as OLEDs and OFETs. In particular, tetraoxa[8]circulenes have been used to prepare discotic liquid crystals, [1] blue organic light-emitting diodes (OLEDs) [2], as well as stable radical cation salts [5], and it has been demonstrated that they aggregate in the solid state and in solution [3].

All tetraoxa[8]circulenes are planar π-extended molecules with a circular system of condensed furan and benzene rings that has a planar cyclooctatetraene ring at the center. Interestingly, all hetero[8]circulenes (octathia[8]circulenes, octaselena[8]circulenes, tetraoxa[8]circulenes, etc.) contain 32 π-electrons in a polycondensed system (Fig. 1a–c).

Therefore, at first glance, hetero[8]circulenes do not conform with the Hückel $4n+2$ rule indicating aromaticity; rather, they comply to the $4n$ ($n=8$) rule indicating antiaromaticity. Neither does the "annulene in annulene" concept apply in this case: the 32 π-electrons in the polycondensed system of a hetero[8]circulene comprises an outer perimeter containing 24 π-electrons and an inner perimeter with 8 π-electrons (Fig. 1b). Actually, however, the Hückel rule is not violated, as it is only strictly valid for monocyclic conjugated systems (annulenes in general)—it is not always true for polycyclic compounds (such as pyrene, benzo[e]pyrene, [8]circulene [8]).

Therefore, we must also use structural, energetic, reactivity, and magnetic criteria to determine the aromaticity of tetraoxa[8]circulenes. The nucleus-independent chemical

Fig. 1 The geometric structure
(**a**) and a schematic of the π-
electronic structure (**b**) of the
simplest symmetric tetraoxa[8]
circulene, and the structure of
the related octathia[8]circulene
(**c**)
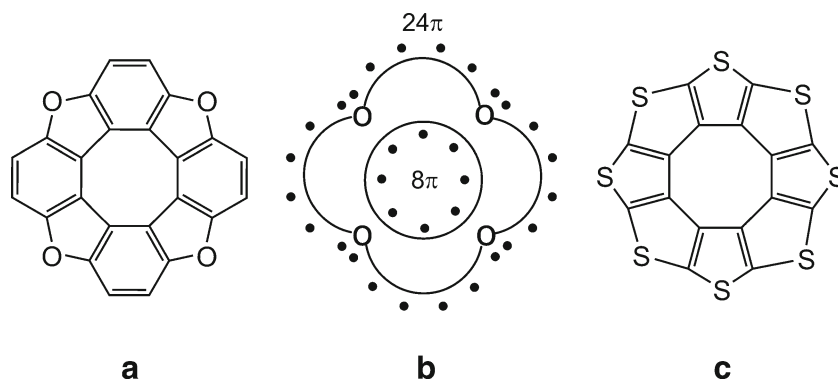
shift (NICS) criterion is the most reliable probe of aromaticity
due to its simplicity and efficiency. An NICS index corre-
sponds to the negative of the magnetic shielding calculated in
the vicinity of the molecule [9]. NICS indices are usually
calculated in the center of the studied ring and at a series of
regularly distributed points along the normal to the ring plane
[9–12]. Negative NICS values in the center of the ring indicate
the presence of induced diatropic ring currents (aromaticity),
whereas positive NICS values at the same points denote para-
tropic ring currents (antiaromaticity) [9].

In the work described in the present paper, we used mag-
netic NICS criteria to qualitatively and quantitatively describe
the aromaticity of tetraoxa[8]circulene molecules. The calcu-
lated NICS values for tetraoxa[8]circulene molecules are com-
pared with well-known data for benzene, furan, and
naphthalene—components of tetraoxa[8]circulene molecules.

Computational details

The equilibrium geometric parameters for the tetraoxa[8]circu-
lene molecules presented in Fig. 2 were calculated by the DFT/
B3LYP [13, 14] method, controlling possible symmetry con-
straints using the double-zeta Dunning type cc-pVDZ [15] basis
set, using the GAUSSIAN 03 package [16]. All vibrational
mode frequencies were found to be real, indicating that a true
minimum was found on the hypersurface of the total energy.
Ghost atoms (Bq) were used to designate the points at which the
NICS parameter was determined. The nuclear magnetic shield-
ing tensors for each atom (including the Bq ghost atoms) of the
tetraoxa[8]circulene, benzene, furan and naphtalene molecules
were calculated with the gauge-independent atomic orbital
(GIAO) approach [17, 18] at the B3LYP/6-311+G(d,p) [19]
level. The NICS indices calculated at the center of each ring
are termed NICS(0) (indicated in bold in Fig. 2). Similarly, the
NICS values at 1 Å above the plane of the ring are denoted NICS
(1) (under the NICS(0) values in Fig. 2). NICS(1) is a recom-
mended measure of the π-electron delocalization [11, 20], while
NICS(0) is considered a gauge of the σ+π-electron delocaliza-
tion. The position of the center of the ring center was found by
obtaining the coordinates of the (3,+1) critical point for the ring

electron density (the electron density gradient at the critical point
is zero by definition), in accordance with a recently published
technique [21]. The analysis of the electron density distribution
function $\rho(r)$ and the search for the coodinates of the critical
point were performed by the QTAIM method [22] using the
AIMQB program, which is implemented in the AIMAll package
[23]. All DFT calculations were performed on a PDC supercom-
puter at the Royal Institute of Technology (Stockholm).

Results and discussion

The application of the magnetic NICS criterion for aromaticity
to the studied tetraoxa[8]circulenes (Fig. 2) is discussed for the
first time in the present work. However, the NICS character-
ization of aromaticity has already been applied to octathia[8]
circulene (sulflower; Fig. 1c), in comparison with free thio-
phene [24, 25]. The aromaticity of related hetero[8]circulenes
was also discussed in some recently published papers [26–28].
In [24], it was shown that the NICS(1) value for the central
cyclooctatetraene ring of the sulflower molecule is positive
and equal to 2.4 ppm, which indicates that the eight-
membered ring is antiaromatic. The NICS(1) value for each
of the eight condensed thiophene rings is negative (−7.1 ppm)
and indicates the presence of π-aromaticity.

The NICS(0) and NICS(1) values for the studied tet-
raoxa[8]circulenes (**a**–**g** in Fig. 2) are positive (similar to those
of sulflower), ranging from 9.23 to 6.55 ppm and from 5.99 to
3.79 ppm, respectively. Note that the NICS(0) values for the
central rings of the tetraoxa[8]circulenes are much lower than
those of the hypothetical highly antiaromatic planar cyclo-
octatetraene molecule (NICS(0)=30.1 ppm [10] at the
B3LYP/6-31 G* level).

From Fig. 2, all benzene rings in the π-extended sys-
tems are characterized by NICS(0) and NICS(1) values
which in the range from −10.53 ppm (**e**) to −7.56 ppm (**b**)
and from −10.06 ppm (**e**) to −7.89 ppm (**b**), respectively.
This values are similar to the NICS(0) and NICS(1) values
of the free benzene molecule (Fig. 3).

By analogy, NICS characterization of the conjugated naph-
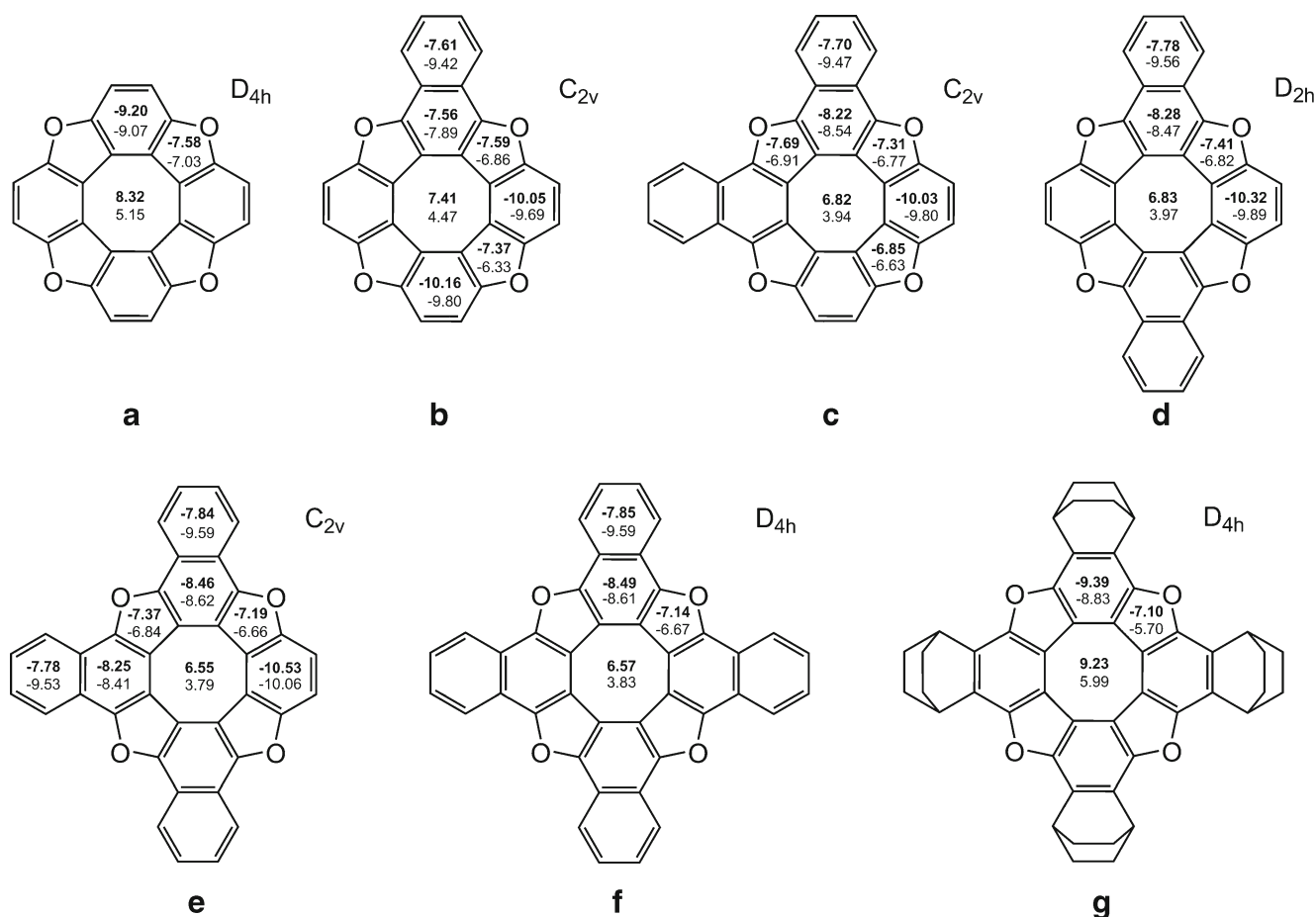thalene fragments yields similar results to those obtained for free

Fig. 2 Structures of the studied π-extended tetraoxa[8]circulenes. The NICS(0) values are indicated in *bold*; the NICS(1) values are presented under the NICS(0) values

naphthalene (Figs. 2 and 3). There are significant differences in the NICS indices of the conjugated furan moieties and those of the free furan molecule (Figs. 2 and 3). This is due to considerable delocalization of the furan π-system into neighboring benzene rings. In this way, a common π-extended system (distributed like a planar ribbon) is formed in the studied tetraoxa[8]circulene molecules. Each ring in this system is characterized by a negative NICS(1) value, which indicates that π-aromaticity dominates during ring circuit creation. It should be noted that our NICS calculations for the benzene, furan, and naphthalene molecules agree well with the recognized data in

[9]. The NICS(0) and NICS(1) values calculated by the B3LYP/6-311+G(d,p) method for the benzene, furan, and naphthalene molecules are −8.03 ppm and −10.2 ppm, −11.88 ppm and −9.38 ppm, and −8.55 ppm and −10.2 ppm, respectively [9] (note that similar values were recently published in [29]). In general, tetraoxa[8]circulenes do obey the structural and ^{1}H NMR spectroscopic criteria for aromaticity. The structural criterion is that the bond lengths in the system of condensed rings are equal, which has been demonstrated in previous publications [30–32]. The ^{1}H chemical shift in the aromatic region of the ^{1}H NMR spectrum of molecule **a** in Fig. 2 occurs at 7.68 ppm, whereas the benzene proton shift occurs at 7.26 ppm [9].

Conclusions

Quantum chemical study of π-extended symmetrical tetraoxa[8]circulene molecules using DFT and QTAIM methods allowed us to find the coordinates of the critical points in the rings, and to calculate the nuclear magnetic shielding tensors at these critical points with dummy Bq ghost atoms
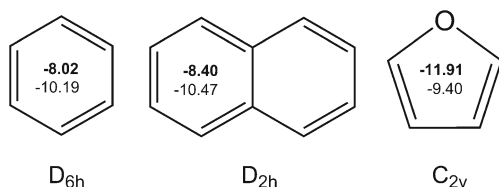

Fig. 3 NICS characterization of the benzene, furan and naphthalene molecules: the NICS(0) values are indicated in *bold*; the NICS(1) values are presented under the NICS(0) values

or real atoms. The calculated shielding tensors and their isotropic components were found to be in good agreement with known values for the benzene, furan, and naphthalene molecules. All of the tetraoxa[8]circulenes studied in the present work consist of two circular conjugated systems. One of these systems is a planar cyclooctatetraene ring, which is typically antiaromatic according to the Hückel $4n$ rule and the calculated NICS(0) and NICS(1) values. The second (outer) ring system is typically aromatic according to the magnetic criterion. This circular π-extended system consists of condensed benzene and furan rings, and looks like a circular flat molecular ribbon.

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