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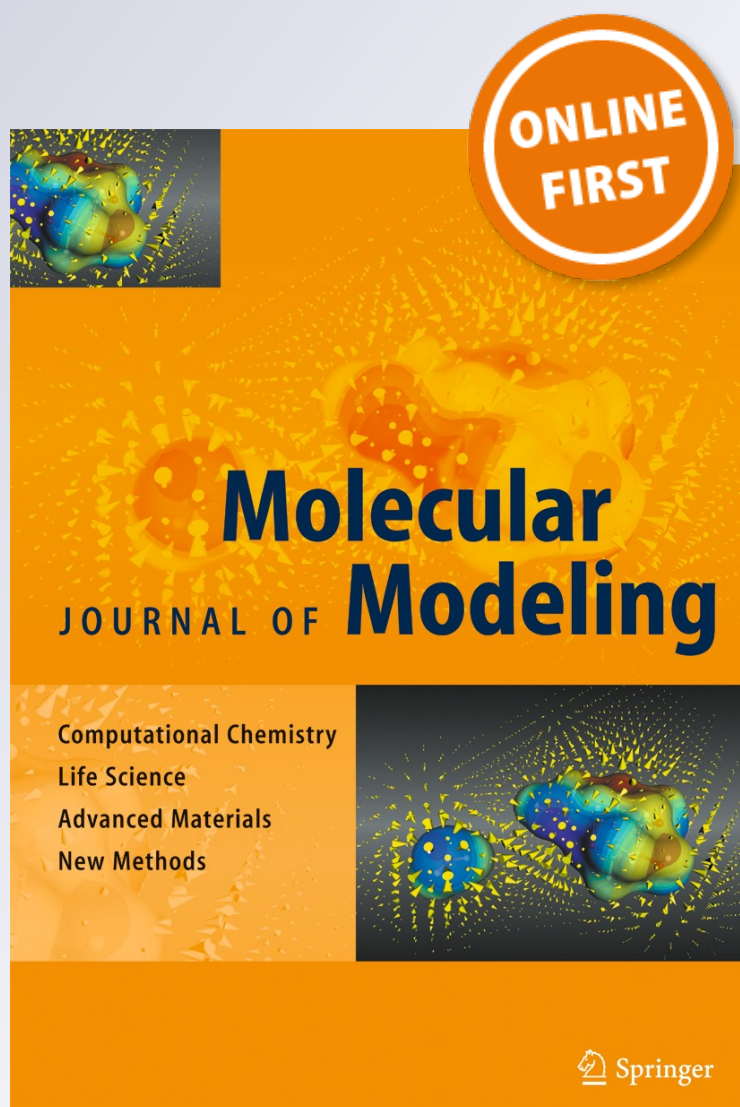
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Nucleus-independent chemical shift criterion for aromaticity in π -extended tetraoxa[8]circulenes

Gleb V. Baryshnikov · Boris F. Minaev · Michael Pittelkow · Christian B. Nielsen · Roberto Salcedo

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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.

Keywords Tetraoxa[8]circulenes · Aromaticity · Antiaromaticity · Hückel rule · NICS indices · Cyclooctatetraene ring

G. V. Baryshnikov (✉) · B. F. Minaev
Bohdan Khmelnytsky National University,
18031 Cherkasy, Ukraine
e-mail: glebchem@rambler.ru

B. F. Minaev
Theoretical Chemistry, School of Biotechnology,
Royal Institute of Technology,
10691 Stockholm, Sweden

M. Pittelkow · C. B. Nielsen
Department of Chemistry, University of Copenhagen,
Universitetsparken 5,
2100 Copenhagen Ø, Denmark

R. Salcedo
Instituto de Investigaciones en Materiales,
Universidad Nacional Autónoma de México,
Circuito Exterior, Ciudad Universitaria, Coyoacán,
04510 Mexico D.F., Mexico

Introduction

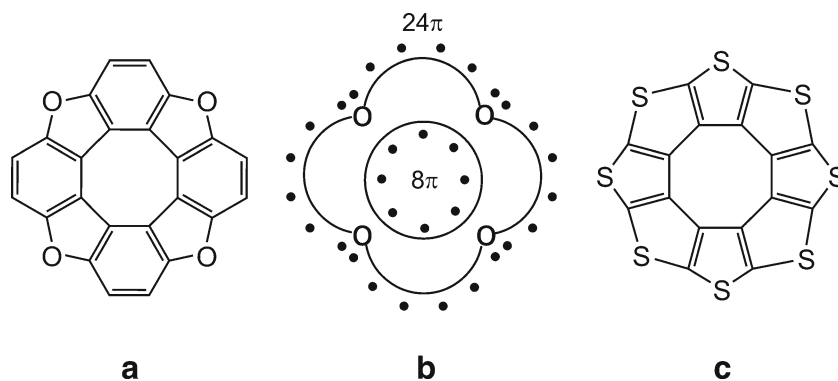
The synthesis and properties of tetraoxa[8]circulenes have attracted significant attention in the past decade [1–5]. Tetraoxa[8]circulenes are highly stable compounds that feature a central eight-membered ring surrounded by four benzene rings and four furan rings in an alternating manner. Both tetraoxa[8]circulenes 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 corresponds 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 paratropic ring currents (antiaromaticity) [9].

In the work described in the present paper, we used magnetic NICS criteria to qualitatively and quantitatively describe the aromaticity of tetraoxa[8]circulene molecules. The calculated NICS values for tetraoxa[8]circulene molecules are compared 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]circulene molecules presented in Fig. 2 were calculated by the DFT/B3LYP [13, 14] method, controlling possible symmetry constraints 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 shielding tensors for each atom (including the Bq ghost atoms) of the tetraoxa[8]circulene, benzene, furan and naphthalene 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 recommended measure of the π -electron delocalization [11, 20], while NICS(0) is considered a gauge of the $\sigma+\pi$ -electron delocalization. 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 coordinates 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 supercomputer 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 characterization of aromaticity has already been applied to octathia[8]circulene (sulflower; Fig. 1c), in comparison with free thiophene [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 tetraoxa[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 cyclooctatetraene molecule (NICS(0)=30.1 ppm [10] at the B3LYP/6-31 G* level).

From Fig. 2, all benzene rings in the π -extended systems 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. These 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 naphthalene fragments yields similar results to those obtained for free

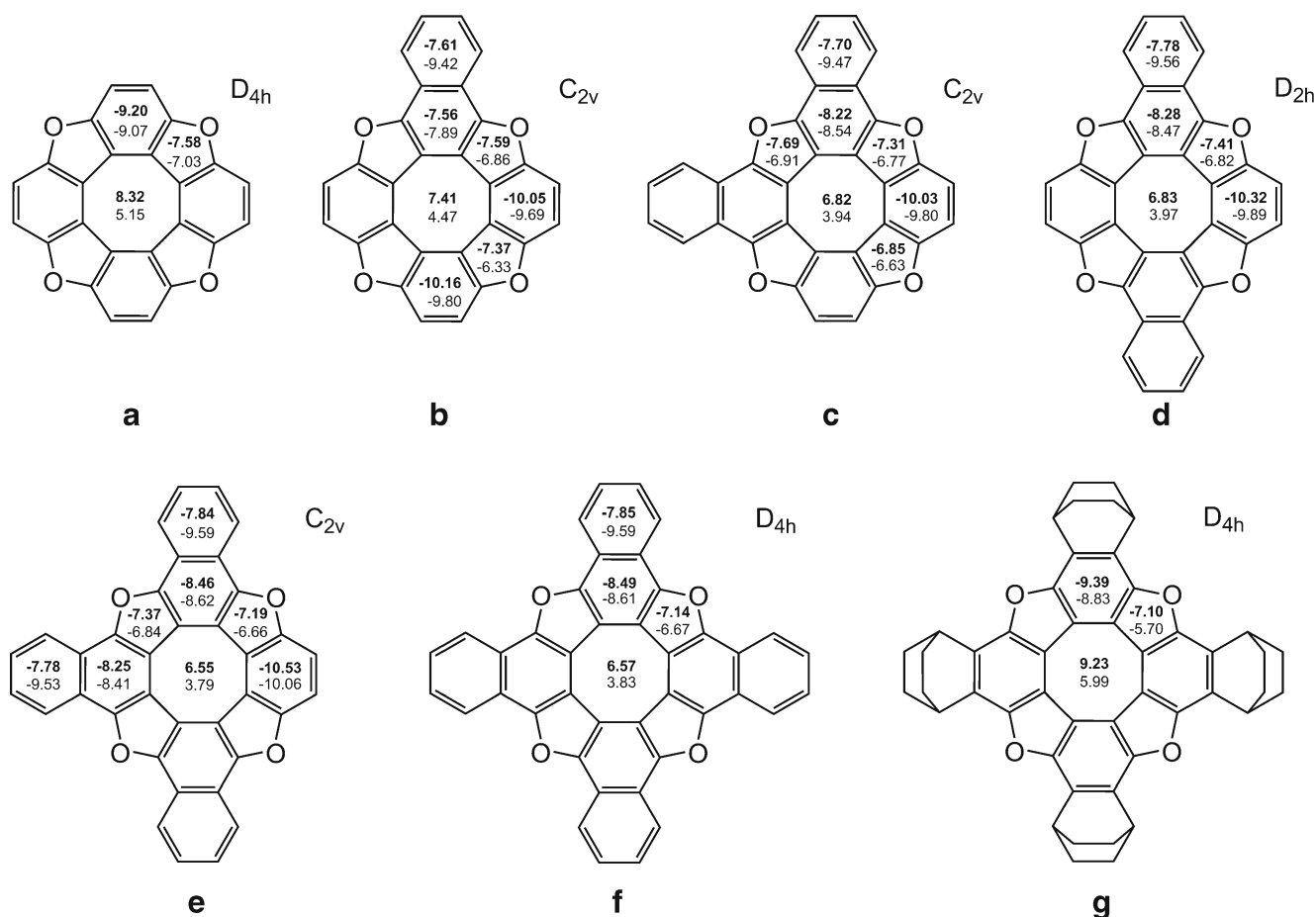


Fig. 2 Structures of the studied π -extended tetraoxa[8]circulenes. The NICS(0) values are indicated in *bold*; the NICS(1) values are presented under the NICS(0) values

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 ^1H 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 ^1H chemical shift in the aromatic region of the ^1H NMR spectrum of molecule **a** in Fig. 2 occurs at 7.68 ppm, whereas the benzene proton shift occurs at 7.26 ppm [9].

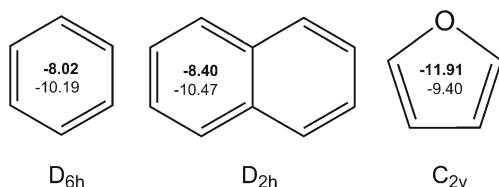


Fig. 3 NICS characterization of the benzene, furan and naphthalene molecules: the NICS(0) values are indicated in *bold*; the NICS(1) values are presented under the NICS(0) values

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

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.

References

- Eskildsen J, Reenberg T, Christensen JB (2000) Substituted tetraoxa[8]circulenes—new members of the liquid crystal family. *Eur J Org Chem* 2000:1637–1640
- Nielsen CB, Brock-Nannestad T, Reenberg TK, Hammershøj P, Christensen JB, Stouwdam JW, Pittelkow M (2010) Organic light-emitting diodes from symmetrical and unsymmetrical π -extended tetraoxa[8]circulene. *Chem Eur J* 16:13030–13034
- Brock-Nannestad T, Nielsen CB, Schau-Magnussen M, Hammershøj P, Reenberg TK, Petersen AB, Trpcevski D, Pittelkow M (2011) Tetra-*tert*-butyltetraoxa[8]circulene and its unusual aggregation behaviour. *Eur J Org Chem* 2011:6320–6325
- Eskildsen J, Hammershøj P, Reenberg TK, Larsen U, Pittelkow M, Leth SM, Peck RA, Christensen JB (2007) Substituted tetraoxa[8]circulenes. *Asian Chem Lett* 11:211–218
- Rathore R, Abdelwahed SH (2004) Soluble cycloannulated tetraoxa[8]circulene derivatives: synthesis, optical and electrochemical properties, and generation of their robust cation–radical salts. *Tetrahedron Lett* 45:5267–5270
- Yu K, Sumerin VV, Shpanchenko RV, Balenkova ES, Nenajdenko VG (2006) “Sulflower”: a new form of carbon sulfide. *Angew Chem Int Ed* 118:7527–7530
- Yu CK, Balenkova ES, Nenajdenko VG (2008) From thiophene to sulflower. *Mendeleev Commun* 18:171–179
- Salcedo R, Sansores LE, Picazo A, Sansón L (2004) [8]Circulene. Theoretical approach. *J Mol Struct (THEOCHEM)* 678:211–215
- Chen Z, Wannere CS, Corminboeuf C, Puchta R, Schleyer PvR (2005) Nucleus-independent chemical shifts (NICS) as an aromaticity criterion. *Chem Rev* 105:3842–3888
- Schleyer PvR, Maerker C, Dransfeld A, Jiao H, Hommes NJRvE (1996) Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. *J Am Chem Soc* 118:6317–6318
- Schleyer PvR, Manoharan M, Wang Z-X, Kiran B, Jiao H, Puchta R, Hommes NJRvE (2001) Dissected nucleus-independent chemical shift analysis of π -aromaticity and antiaromaticity. *Org Lett* 3:2465–2468
- Fallah-Bagher-Shaidaei H, Wannere CS, Corminboeuf C, Puchta R, Schleyer PvR (2006) Which NICS aromaticity index for planar π rings is best? *Org Lett* 8:863–866
- Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652
- Lee C, Yang W, Parr RG (1988) Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789
- Dunning TH (1989) Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J Chem Phys* 90:1007–1023
- Frisch M, Trucks G, Schlegel H, Scuseria G, Robb M, Cheeseman J, Montgomery J, Vreven J, Kudin K, Burant J, Millam J, Iyengar S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox RJ, Hratchian H, Cross J, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R, Yazyev O, Austin A, Cammi R, Pomelli C, Ochterski J, Ayala P, Morokuma K, Voth G, Salvador P, Dannenberg J, Zakrzewski V, Dapprich S, Daniels A, Strain M, Farkas O, Malick D, Rabuck A, Raghavachari K, Foresman J, Ortiz J, Cui Q, Baboul A, Clifford S, Cioslowski J, Stefanov B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R, Fox D, Keith T, Al-Laham M, Peng C, Nanayakkara A, Challacombe M, Gill P, Johnson B, Chen W, Wong M, Gonzalez C, Pople J (2004) Gaussian 03, revision C.02. Gaussian, Inc., Wallingford
- London F (1937) Théorie quantique des courants interatomiques dans les combinaisons aromatiques. *J Phys Radium* 8:397–409
- Cheeseman JR, Trucks GW, Keith TA, Frisch MJ (1996) A comparison of models for calculating nuclear magnetic resonance shielding tensors. *J Chem Phys* 104:5497–5509
- McLean AD, Chandler GS (1980) Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, $Z=11-18$. *J Chem Phys* 72:5639–5648
- Schleyer PvR, Jiao H, Hommes NJRvE, Malkin VG, Malkina OL (1997) An evaluation of the aromaticity of inorganic rings: refined evidence from magnetic properties. *J Am Chem Soc* 119:12669–12670
- Foroutan-Nejad C, Shahbazian S, Feixas F, Rashidi-Ranjbar P, Solà MAA (2011) Dissected ring current model for assessing magnetic aromaticity: a general approach for both organic and inorganic rings. *J Comput Chem* 32:2422–2431
- Bader RFW (1990) *Atoms in molecules. A quantum theory*. Clarendon, Oxford
- Keith TA (2010) AIMAll, version 10.07.25. <http://www.aim.tkgristmill.com>
- Bukalov SS, Leites LA, Lyssenko KA, Aysin RR, Korlyukov AA, Zubavichus JV, Chernichenko KY, Balenkova ES, Nenajdenko VG, Antipin MY (2008) Two modifications formed by “sulflower” $C_{16}S_8$ molecules, their study by XRD and optical spectroscopy (Raman, IR, UV-Vis) methods. *J Phys Chem A* 112:10949–10961
- Gahungu G, Zhang J (2008) Shedding light on octathio[8]circulene and some of its plate-like derivatives. *Phys Chem Chem Phys* 10:1743–1747
- Gribanova TN, Zefirov NS, Minkin VI (2009) Quantum-chemical study of heteroanalogues of [8]circulenes and their derivatives. *Dokl Chem* 426:105–110
- Gribanova TN, Zefirov NS, Minkin VI (2010) Structure and stability of the heteroannulated [8–10]circulenes: a quantum-chemical study. *Pure Appl Chem* 82:1011–1024
- Napoleon B, Hagelberg F, Huang M-J, Watts JD, Simeon TM, Vereen D, Walters WL, Williams QL (2011) Theoretical investigation into the structural, thermochemical, and electronic properties of the decathio[10]circulene. *J Phys Chem A* 115:8682–8690
- Andjelković L, Perić M, Zlatar M, Grubišić S, Gruden-Pavlović M (2012) Magnetic criteria of aromaticity in a benzene cation and anion: how does the Jahn–Teller effect influence the aromaticity? *Tetrahedron Lett* 53:794–799
- Minaev BF, Baryshnikov GV, Minaeva VA (2011) Density functional theory study of electronic structure and spectra of tetraoxa[8]circulenes. *Comp Theor Chem* 972:68–74
- Minaeva VA, Minaev BF, Baryshnikov GV, Agren H, Pittelkow M (2012) Experimental and theoretical study of IR and Raman spectra of tetraoxa[8]circulenes. *Vib Spectrosc* 61:156–166
- Radenković S, Gutman I, Bultinck P (2012) A comparative study of aromaticity in tetraoxa[8]circulenes. *J Phys Chem A* 116:9421–9430. doi:10.1021/jp307281y