

Influence of conformation on the electronic structure of thiacalixarenes according to DFT calculations and X-ray emission spectroscopy

Gennady A. Kostin^{a,b,*}, Natalya A. Kryuchkova^{a,b}, Lev N. Mazalov^{a,b}, Vladislav G. Torgov^a, Andrej B. Drapaylo^c

^a Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Av. Lavrentyeva, 3, 630090 Novosibirsk, Russia

^b Novosibirsk State University, Pirogova Str., 2, 630090 Novosibirsk, Russia

^c Institute of Organic Chemistry, National Academy of Sciences, Murmanskaya Str., 5, 02660 Kiev, Ukraine

ARTICLE INFO

Article history:

Received 5 August 2011

Received in revised form 29 September 2011

Accepted 29 September 2011

Available online 8 October 2011

Keywords:

Thiacalixarene

DFT calculation

X-ray emission spectroscopy

Electrophilic substitution

ABSTRACT

The DFT calculations of different thiacalix[4]arenes show that the conformation and geometry of arene core mainly determine the difference in electronic density distribution (frontier occupied MO and ESP charges) between “cone” and “1,3-alternate” conformation. The key factor is orientation of benzene rings relative to average plane through bridging sulfur atoms. Calculated structure of frontier orbitals was verified by experimental sulfur K_{β} spectra, calculated spectra reproducing main features of experimental ones. Difference in HOMO and ESP distribution on carbon atoms in benzene rings for “cone” and “1,3-alternate” conformers correlates with earlier reported data on regioselectivity of electrophilic substitution in these compounds.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Thiacalixarenes (TCAs) is a relatively new class of macrocyclic compounds, which were actively studied in recent years. The replacement of the bridging CH_2 groups by electron-withdrawing sulfur atoms leads to a substantial difference between TCAs and classic calixarenes [1–3]. Several features of TCA such as increased acidity of OH groups or the possibility of directly replacing them by amino and amide groups [1,4] can be qualitatively explained by the inductive effects of the more electronegative sulfur atoms. The unusual regioselectivity of electrophilic substitution in TCA (Scheme 1) and its dependence on the conformation reported in Lhotak's recent papers [5–8] require a quantitative description of the highest occupied molecular orbitals and the charge distribution on the carbon atoms in the benzene rings.

From the viewpoint of coordination chemistry, the major distinction of TCA is the presence of sulfur atoms as additional donor centers. The coordination chemistry of classic calixarenes without additional donor groups is limited to phenoxo and π -complexes. The sulfur atoms of TCA can participate in complexation either together with OH groups or as single donor atoms, especially for chalcophile metals. The possibility of their participation in com-

plexation is determined by the geometrical characteristics of thiacalixarenes, the electron density on the sulfur atoms, and the contribution of the valence electrons of sulfur to the highest occupied molecular orbitals. If TCA is modified by adding donor groups to the upper or lower rim, the electron interference between the groups should also be taken into consideration. The participation of the valence S 3p AO in the highest occupied molecular orbitals can be experimentally proven by X-ray emission spectroscopy (3p valence-to-1s-core XES, K_{β} -line). The XES spectra of TCAs obtained earlier [9] revealed a systematic difference between TCAs in the “cone” and “1,3-alternate” conformations, which was evidence of different sulfur contributions to HOMO.

The experimental studies should be complemented with a profound theoretical description of the electronic structure of TCA. This study is focused on the interrelationships between the electronic structures of TCAs, their reactivities in electrophilic substitution reactions, and X-ray spectra.

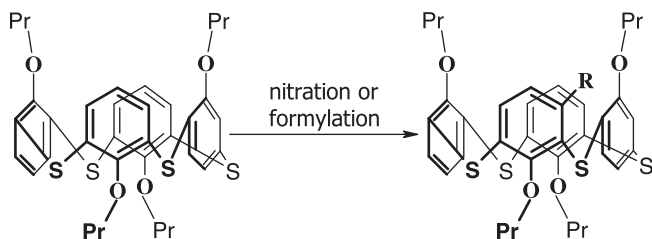
Previous quantum chemical calculations of TCAs were mainly focused on the energy aspects of complexation with different metals [10–13]. A qualitative description of HOMO for TCA in the “cone” and “1,3-alternate” conformations was given in [8,10].

2. Experimental

Thiacalix[4]arenes **1–6** (Scheme 2) were synthesised as described in [14–18]. Model compounds **7**, **8** were not synthesised,

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, av. Lavrentyeva, 3, 630090 Novosibirsk, Russia.

E-mail address: kostin@niic.nsc.ru (G.A. Kostin).



Scheme 1.

but DFT calculations were performed to compare the results with those for **1** and **5**. The S K_{β} X-ray fluorescence emission spectra of **1–6** were recorded on a “Stearate” X-ray ultrasoft spectrometer. The X-ray tube operating conditions were $V = 8$ kV, $I = 100$ mA. A (1340) quartz crystal was used as a crystal analyzer. The compounds were deposited on the secondary anode of the X-ray tube. The spectra were measured at the liquid nitrogen temperature. The spectrometer resolution in the studied region was $\sim 5 \times 10^3$.

The electronic structures of synthesised thiacalix[4]arenes in the “cone” (**1–4**) and “1,3-alternate” (**5, 6**) conformations and of model compounds (**7, 8**) were calculated using the Jaguar 6.5 program, Shrodinger Inc. [19]. The geometry of thiacalix[4]arene molecules was optimized by the DFT technique with the B3LYP hybrid exchange-correlation functional [20,21]. The M6-31G(TM)* basis set [22] was used for all atoms.

3. Results and discussion

Table 1 shows the selected interatomic distances, interatomic angles, and interplanar angles for the optimized structures of the molecules. The calculated average bond lengths (S–C, C–O) and C–S–C bond angles are close for all structures and are in reasonable agreement with the experimental data for the crystal phases (the experimental parameters from the original papers or calculated from the corresponding CIF files in CCDC are given in parentheses). For all “1,3-alternate” structures **5–7**, the angles between the average plane through four sulfur bridging atoms $[S_4]$ and the planes of the benzene rings are approximately 90° , the structure of the arene core being of approximately D_{2d} symmetry. In “cone” conformers **1–4** with OH groups in the lower rim, the calculated interplanar angles vary from 26° to 70° . The calculated structure of **1** has approximately C_{4v} symmetry, the interplanar angle (51.3 – 52.8°) being the average between the two experimental values corresponding to the “pinched cone” structure determined by single crystal XRD [14]. Due to the presence of substituents in the upper rim of **2–4**, the symmetry is lowered from C_{4v} to the “pinched cone” conformation. As thiacalixarenes tend to include small molecules in the inner cavity, the experimental interplanar angles for **2** depend on the nature of the included molecule [23,24]. The calculated values shown in Table 1 are closest to those reported for the structure of a pyridine inclusion compound [23]. The optimized

structure of **8** is “pinched cone” with C_{2v} symmetry common to TCA in the “cone” conformation tetraalkylated in the lower rim [14,25].

3.1. Molecular orbitals and XES spectra

The molecular orbital diagram for thiacalix[4]arene **5** in the “1,3-alternate” conformation is shown along with the typical MO schemes in Fig. 1. Four highest occupied orbitals (from HOMO to HOMO-3) are mainly formed from the 3p orbitals of the sulfur atoms and involve the π -bonding orbitals of the benzene rings, the total contribution of all sulfur AOs being 40–70%. The orbitals from HOMO-4 to HOMO-7 are mainly distributed on the carbon atoms of the benzene rings (65–75%) with some contribution from the oxygen and sulfur atomic orbitals. For orbitals from HOMO to HOMO-4, the electron density distribution on the carbon atoms is determined by the «2 + 2» π -bonding orbitals of the benzene ring (Scheme 3). The electron density determined by HOMO-3, 7, and 8 is mainly located on the carbon atoms bonded to the OR group (C1) and in the *para*-position (C4), the carbon 2p AO forming the «3 + 3» π -bonding orbitals of the benzene ring (Scheme 3). For the doubly degenerate orbitals (HOMO-1, 2 and HOMO-5, 6), one pair of opposite benzene rings have the same electron density distribution as in the “2 + 2” orbital and the other as in the “3 + 3.” The 2p orbitals of the oxygen atoms participate in the formation of molecular orbitals starting from HOMO-9 to lower-lying ones. The total contribution of the atomic orbitals of all four oxygen atoms to the highest occupied molecules orbitals does not exceed 13%. For “1,3-alternate” **7** with OH instead of methoxy groups, the structure of the molecular orbitals changes but slightly. The orbitals that are close in energy are inverted (HOMO-4 of b_1 symmetry and HOMO-5, -6 of e symmetry), but the contributions of atomic orbitals to different HOMOs coincide well with the results obtained for **5**.

The highest occupied molecular orbital of **1** (Fig. 2), having b_2 symmetry, corresponds to the linear combination of the “3 + 3” π -bonding orbitals of the benzene rings (70%) and the 2p atomic orbitals of the oxygen atoms (27%). Although the oxygen 2p orbitals in HOMO are perpendicular to the benzene plane, they have different phase signs, thus forbidding the π -p bonding. The contribution of the sulfur AO to HOMO is negligible. The doubly degenerate HOMO-1 and HOMO-2 have similar structures, each orbital being distributed on only two of the four benzene rings. The HOMO-3, HOMO-5, and HOMO-6 are the linear combinations of mainly 3p sulfur atomic orbitals, the total contribution of all sulfur AOs being 70–80%. The occupied molecular orbitals that are lower in energy are formed by the «2 + 2» π -bonding orbitals of the benzene rings with a contribution from the 3p (3s) sulfur orbitals, the total contribution of the sulfur AOs varying from 21 to 42%. The positive overlap of the S_{3p} orbitals with the π -bonding orbitals of the benzene ring in HOMO-7 and HOMO-8 leads to additional S–C π -bonding. It is interesting to note that for thiacalixarene **8** in the “pinched cone” conformation, molecular orbitals from HOMO to HOMO-3 are similar in shape to the orbitals of TCA in the “1,3-alternate” conformation (Fig. 1) and mainly formed from the sulfur atomic orbitals (50–60%). The doubly degenerate HOMO-4 and -5 in TCA **8** are primarily localized on the benzene rings orientated outwardly relative to the cavity of TCA, the electron density being maximum on the C1 and C4 carbon atoms. As in the case of **5**, in TCA **8** the oxygen atomic orbitals make a considerable contribution (20–55%) only to HOMO-9 and lower-energy orbitals (HOMO-10 to -12).

The optimized geometry of phosphorylated TCA **4** differs substantially from C_{4v} symmetry, and this is also responsible for the less symmetric character of HOMO (Fig. 3). The structure of the occupied orbitals in **4**, however, is similar that in **1** (“cone”). The highest occupied molecular orbital is a linear combination of

	Y	X	
	H	H	cone
1	H	H	cone
2	H	t-Bu	cone
3	H	CH ₂ PO(Ph) ₂	cone
4	H	CH ₂ PO(OEt) ₂	cone
5	Me	H	1,3-alt
6	Bu	H	1,3-alt
7	H	H	1,3-alt
8	Me	H	cone

Scheme 2.

Download English Version:

<https://daneshyari.com/en/article/1410108>

Download Persian Version:

<https://daneshyari.com/article/1410108>

[Daneshyari.com](https://daneshyari.com)