Tetrahedron Letters 54 (2013) 1510–1514

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A 3D supramolecular network assembly based on thiacalix[4]arene by halogen–halogen, CH–Br, CH–π, and S–π interactions

Manabu Yamada [a,*], Yuji Ootashiro [b], Yoshihiko Kondo [b], Fumio Hamada [b,*]

[a] Center for Geo-Environmental Science (CGES), Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan
[b] Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan

ARTICLE INFO

Article history:
Received 16 November 2012
Revised 19 December 2012
Accepted 26 December 2012
Available online 3 January 2013

Keywords:
Calixarenes
Thiacalixarenes
Halogen–halogen interactions
Crystal structure

ABSTRACT

We have elucidated an interesting architecture via assembling each of 5,11,17,23-tetrabromo-25,26,27,28-tetrabutoxythiacalix[4]arene molecules in the crystalline state. 5,11,17,23-Tetrabromo-25,26,27,28-tetrabutoxythiacalix[4]arene molecules resulted in a 3D supramolecular assembly through halogen–halogen interactions and further CH–π and S–π interactions by both the crystallographic and computational approaches.

Supramolecular assemblies involving specific interactions between designed molecules and guest molecules have been shown to exhibit a variety of supramolecular functionalities.[1] Noncovalent intermolecular forces involved in the formation of these supramolecular assemblies, such as hydrogen bonding, van der Waals interactions, and the metal coordination of ligating groups of the molecular hosts, play an important role in the supramolecular assembly and molecular recognition occurring in supramolecular systems and living systems.

To date, a wide array of supramolecular architectures have been produced, demonstrating the possibility of creating new materials with intriguing architectures such as nanoscale capsules[2] and cage structures[3] in solution and in the solid state. In these assemblies, nanoscale capsules and hexameric architectures made up of macrocyclic hosts such as calixarenes,[4] resorcinarenes,[5] pyrogallolarenes,[6] and their numerous variants[7] have been intensively investigated in terms of their structures, functions, and the combinations of host and guest molecules in their architectures. These supramolecular assemblies have great potential for selective guest encapsulation, drug delivery, transport, and catalysis in many applications, since the interior spaces can be functionalized to achieve different desirable functions.

Although these assembles are generally built up through common noncovalent interactions such as hydrogen bonding or metal coordination to the ligating groups of the molecular hosts, halogen–halogen interactions are also important noncovalent interactions in the formation of supramolecular architectures, as has been demonstrated by the weak intermolecular forces used in crystal engineering.[8] However, halogen–halogen interactions are rare in the formation of supramolecular assemblies of macrocyclic compounds.[9] To our knowledge, no such 3D supramolecular network assembly consisting of only macrocyclic host molecules based on halogen–halogen interactions has been reported in the chemistry of calixarenes and thiacalixarenes.

Herein, we show for the first time that a 3D supramolecular network assembly based on the 5,11,17,23-tetrabromo-25,26,27,28-tetrabutoxy-thiacalix[4]arene **1** (Scheme 1 and see Supplementary data for Experimental Section) is formed from an infinite open network structure consisting of two trimeric units via a halogen–halogen interaction and is further supported by CH–Br, CH–π, and S–π interactions between the infinite open network structures in the crystalline state. We also introduce computational evidence for the halogen–halogen interactions within the assembly.

Single crystals of **1** suitable for single-crystal X-ray diffraction studies were obtained from chloroform/cyclohexane (1:1 v/v) mixed solution over a period of a week.[10] The guest-free crystals of **1** were colorless block crystals with the trigonal space group *R*3*c*, where the asymmetric unit was composed of one thiacalixarene molecule. The crystal itself is an enantiomer of thiacalixarene molecules **1** (Fig. 1a and b). The enantiomeric structure has the same functional groups located at the same positions. However, the stereostructures of each molecule have a bilaterally symmetric

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* Corresponding authors. Tel.: +81 18 889 2442; fax: +81 18 837 0404 (M.Y.); tel.: +81 18 889 2440; fax: +81 18 837 0404 (F.H.).

E-mail addresses: myamada@gipc.akita-u.ac.jp (M. Yamada), hamada@gipc.akita-u.ac.jp (F. Hamada).

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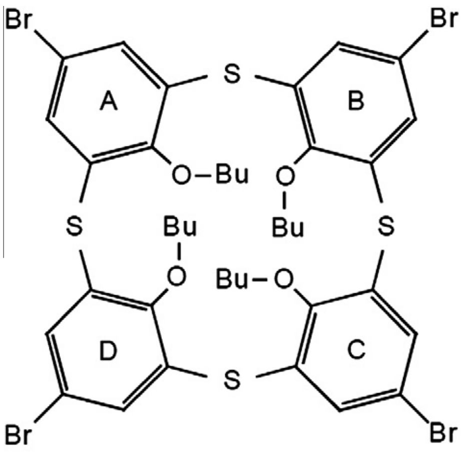
http://dx.doi.org/10.1016/j.tetlet.2012.12.102



1

Scheme 1. Molecular structure of 5,11,17,23-tetrabromo-25,26,27,28-tetrabutoxy-thiacalix[4]arene, **1**.

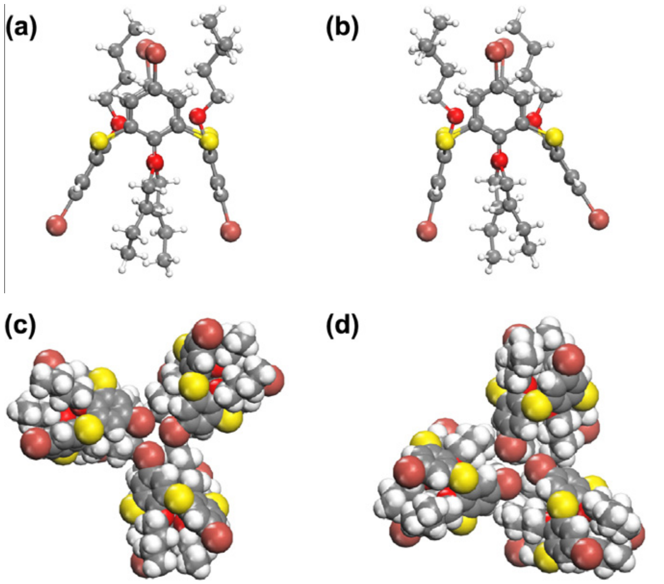


Figure 1. (a), (b) Ball-and-stick diagrams showing the enantiomer of **1**. Space-filling representation of (c) trimer A and (d) trimer B viewed along the [1 1 0] plane. Br = dark red, S = yellow, O = red, C = gray, and H = white.

relationship that depends on the location of the functional groups on upper and lower rims of **1** (see the Supplementary data for Fig. S1). Within this unit, **1** stabilizes in a 1,3-alternate conformer, which includes one disordered butyl group at the D aromatic ring (see the Supplementary data for atomic numbering). The neighboring A and D aromatic rings are slightly flipped inward, whereas the neighboring B and C aromatic rings are slightly flipped outward (see the Supplementary data for Fig. S2). The enantiomer of thiacalixarene molecules **1** shows skewed molecular structures that act as an important building block in the formation of the 3D supramolecular network assembly. Symmetry expansion of the crystal structure of **1** reveals that the two trimeric units held together by halogen–halogen interactions between each of thiacalixarene molecules (Fig. 1c and d). Two trimeric units have a C_3 symmetry axis with the thiacalixarene molecules located around it. Two types of trimers, trimer A and trimer B, can be viewed along the [1 1 0] direction, and each is made up of three skewed subunits of **1** rotated 120° along the *c* axis with respect to each other. Halogen–halogen interactions have been broadly-defined as arising from the different polarizations and dispersion–repulsion interactions in the crystalline states, where anisotropic halogen atoms bonded to sp, sp^2, and/or sp^3 carbon atoms have ellipsoid shapes because of polar flattening effects.[8] There are two types of halogen–halogen interactions, namely Type I and Type II. C–X···X–C contacts (X = halogen atoms) are considered halogen–halogen interactions when their interhalogen distances are less than the sum of van der Waals radii because of an attractive X$^{\delta+}$···X$^{\delta-}$ interaction. In addition, two types of halogen–halogen interactions are based on the two angles centered on the halogen atoms (see Supplementary data for Fig. S3). Preferable angles are Type I ($\theta_1 = \theta_2 = 140$–$180°$) and Type II ($\theta_1 = 150$–$180°$, $\theta_2 = 90$–$120°$). Similarly, a triangular interhalogen interaction is the triangular X_3 synthon, which is a trigonal array of halogen atoms with attractive electrophile–nucleophile Type II contacts. The crystals observed here contain these triangular X_3 synthons with Type II, indicating that the anisotropic bromine atoms of **1** have ellipsoid shapes (see Supplementary data for Fig. S4), as was observed in the previous studies of halogen–halogen interactions.[8] Therefore, as shown in the crystal structure, within each trimer the individual A or D bromo groups of each thiacalixarene molecules induce the formation of the triangular Br_3 synthons between each of the three neighboring thiacalixarene molecules. The Br–Br distances and angles are 3.660 Å and 60°, θ_1 angle is 172.88°, and θ_2 angle is 124.47° in trimer A. The Br–Br distances and angles are 3.699 Å and 60°, θ_1 angle is 166.36°, and θ_2 angle is 116.18° in trimer B (Fig. 2 and see Supplementary data for Fig. S5). The reasons for the formation of the two different trimeric structures are the skewed molecular structures and the increased opportunity for Br–Br contacts in the guest-free crystals of **1**. Interestingly, in trimer A, the θ_2 angle is slightly outside the angle range for Type II, and the observed CH–Br interaction (the CH···Br distance is 3.011 Å) can be attributed to the closeness of the A bromine atoms and the adjacent B methylene groups. Thus, trimer A is sterically hindered from forming ideal halogen–halogen interactions by the *n*-butyl groups, as compared with the stereostructure of trimer B. As will be explained in the computational approach, the structural stability of each trimer is important in the formation of the 3D supramolecular network assembly.

Surprisingly, this system forms an infinite open network structure along the [1 1 0] plane by triangular X_3 halogen–halogen interactions, in which the thiacalixarene molecule alternatively belongs to both two trimeric units using different A or D bromo groups of **1** (Fig. 3). Moreover, the infinite open network structure builds up a 3D supramolecular network assembly by piling up along the *c* axis (Fig. 4). There are three interactions stabilizing the 3D supramolecular network assembly (see the Supplementary data for Fig. S6): (1) aromatic-H–Br interactions from A bromine atoms of base infinite open network structure to D aromatic hydrogen atoms of adjacent infinite open network structure (CH···Br distance of 2.896 Å), (2) CH–π interactions between aromatic rings of base infinite open network structure and hydrogen atoms of the butyl groups of adjacent infinite open network structure (CH···centroid distances of 2.717 and 2.952 Å), and (3) S–π interactions between the bridging sulfur atoms of base infinite open network structure and the aromatic rings of adjacent infinite open network structure (S···centroid distances of 3.593 and 3.765 Å; see Supplementary data for Fig. S7).[11,12] Thus, the crystals of **1** formed from the skewed 1,3-alternate molecular structure have the supramolecular assembly with triangular halogen–halogen interactions between the trimeric units and CH–Br, CH–π, and S–π interactions between the infinite open network structures.

To further elucidate these observed halogen–halogen interactions, we employed a computational approach to investigate the