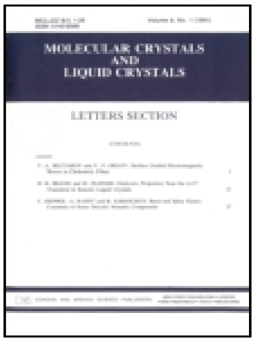

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis and supramolecular interactions involved in the crystal structure of (2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6, 14-thiacycloocta[1,2-b:5,6-b’]diquinoline)$_2$·(1,1,2,2-tetrachloroethane) inclusion compound

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To cite this article: Solhe F. Alshahateet (2016) Synthesis and supramolecular interactions involved in the crystal structure of (2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6, 14-thiacycloocta[1,2-b:5,6-b’]diquinoline)$_2$·(1,1,2,2-tetrachloroethane) inclusion compound, Molecular Crystals and Liquid Crystals, 625:1, 186-194, DOI: 10.1080/15421406.2015.1069445

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1069445

MOL. CRYST. LIQ. CRYST.
2016, VOL. 625, 186–194
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Synthesis and supramolecular interactions involved in the crystal structure of (2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6,14-thiacycloocta[1,2-*b*:5,6-*b*′]diquinoline)$_2$·(1,1,2,2-tetrachloroethane) inclusion compound

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ABSTRACT

The tetrahalo aryl inclusion host 2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6,14-thiacycloocta[1,2-b:5,6-b′]diquinoline 3 was re-synthesized to explore its ability to trap toxic polychlorinated hydrocarbons such as 1,1,2,2-tetrachloroethane (TCE) in the form of host–guest compound. Host 3 crystallizes from a fresh sample of TCE to form an inclusion compound of the formula $(3)_2$·(TCE) in triclinic system, space group P-1, with a = 7.7732(16) Å, b = 10.739(2) Å, c = 14.816(3) Å, $\alpha = 97.329(4)°$, $\beta = 98.619(4)°$, $\gamma = 103.359(4)°$, V = 1172.7(4) Å^3, and Z = 2. The X-ray crystal structure of the $(3)_2$·(1,1,2,2-TCE) is described and analyzed in terms of crystal engineering and supramolecular chemistry. The hosts assemble by means of different types of packing motifs. The included TCE molecules are enclosed within host molecular pens. Novel halogen···halogen intermolecular interactions as well as other non-covalent intermolecular interactions involved in the crystal structure are presented and proved to play an important role in linking these host–host, host–guest, and guest–guest building blocks.

KEYWORDS
Halogen···halogen intermolecular interactions; host–guest system; non-covalent intermolecular interactions; 2; 4; 10; 12-tetrabromo-6; 7; 14; 15-tetrahydro-6; 14-thiacycloocta[1; 2-b:5; 6-b′]diquinoline; 1; 1; 2; 2-tetrachloroethane (TCE); X-ray single crystal structure

Introduction

The use of non-covalent interactions and molecular recognition was extended to many fields, including applications in the analysis of technically, medically, and environmentally important chemical compounds, their separation, purification, and removal and the design of new materials [1]. 1,1,2,2-Tetrachloroethane (TCE) is derived from ethane through a chlorination reaction, and has the highest solvent power of any chlorinated hydrocarbon in addition to its use as intermediate in many industrial productions of chlorinated hydrocarbons. However, it is no longer used due to concerns about its toxicity. Recently, our research group has been interested in developing, synthesizing, and investigating the V-shaped halogenated diheteroaromatic molecules that behave as lattice inclusion hosts that lack the ability to use strong hydrogen bonding in their crystal structures. Instead, their host–guest self-assembly employs a wide variety of weaker intermolecular interactions [2–11].

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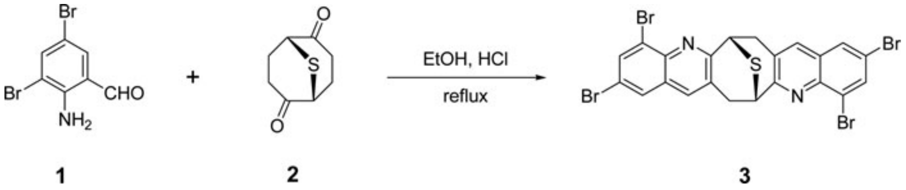


Scheme 1. Synthetic route for 2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6,14-thiacycloocta[1,2-b:5,6-b']diquinoline **3.**

In this paper, the racemic V-shaped host 2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6,14-thiacycloocta[1,2-b:5,6-b']diquinoline **3** was re-synthesized (Scheme 1) and its inclusion ability toward TCE was examined, and it was revealed that the host compound **3** formed lattice inclusion compound of the formula $(\mathbf{3})_2\cdot$(TCE) upon direct crystallization from TCE, its solid-state structure was studied by X-ray single crystal technique, analyzed and presented in terms of crystal engineering and supramolecular chemistry.

Experimental

Synthesis of 2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6,14-thiacycloocta-[1,2-b:5,6-b']diquinoline 3

The target host compound **3** was re-synthesized according to our published procedure [7]. The Friedländer reaction [12,13] was used to obtain compound **3** through the condensation of two equivalents of 2-amino-3,5-dibromobenzaldehyde **1** (available from the Sigma-Aldrich Company), and one equivalent of 9-thiabicyclo[3.3.1]nonane-2,6-dione **2** [14,15] under acidic conditions to afford compound **3** in 57% yield (Scheme 1).

Solution and refinement of the lattice inclusion crystal structure

The single crystal X-ray diffraction experiments were carried out on a Bruker SMART APEX 1000 diffractometer equipped with a CCD detector and Mo Kα sealed tube at 223(2) K. SMART [16] was used for collecting frames data, indexing reflection, and determination of lattice parameters. SAINT [16] was used for integration of intensity of reflections and scaling. SADABS [17] was used for absorption correction, and SHELXTL [18] was used for space group and structure determination and least-square refinements on F^2. All C–H hydrogen atoms were placed in calculated positions for the purpose of structure factor calculation.

Crystallographic data (CIF) have been deposited with the Cambridge Crystallographic Data Centre (CCDC reference number 1008198). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 144(0)-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk). See http://www.rsc.org/suppdata/ce/b4/b418773c/ for crystallographic data in CIF or other electronic format.

Table 1. Crystallographic parameters for $(\mathbf{3})_2\cdot$(TCE) lattice inclusion compound.

CCDC reference number	1008198	
Empirical formula	$(C_{22}H_{12}Br_4N_2S_1)_2\cdot(C_2H_2Cl_4)$	
Formula weight	739.95 gm/mol	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 7.7732(16)$ Å	$\alpha = 97.329(4)°$
	$b = 10.739(2)$ Å	$\beta = 98.619(4)°$
	$c = 14.816(3)$ Å	$\gamma = 103.359(4)°$
Volume	1172.7(4) $Å^3$	
Z	2	
Density (calculated)	2.096 mg/m^3	
Absorption coefficient	7.197 mm^{-1}	
F(000)	710	
Crystal size	$0.40 \times 0.28 \times 0.10$ mm^3	
θ-range for data collection	1.41 to 27.50°.	
Index ranges	$-10 \le h \le 10, -13 \le k \le 13, -19 \le l \le 19$	
Reflections collected	14,924	
Independent reflections	5350 [R(int) = 0.0581]	
Completeness to $\theta = 27.50°$	99.6%	
Absorption correction	SADABS [17]	
Max. and min. transmission	0.5330 and 0.1609	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5350/0/289	
Goodness-of-fit on F2	1.052	
Final R indices [$I > 2\sigma$ (I)]	R1 = 0.0560, wR2 = 0.1620	
R indices (all data)	R1 = 0.0690, wR2 = 0.1716	
Largest diff. peak and hole	2.889 and −0.919 e.$Å^{-3}$	

Results and discussion

Crystal structure of $(3)_2\cdot$(TCE)

In this paper, the X-ray crystal structure of the TCE inclusion compound is discussed. Numerical details of the solution and refinement of the structure are presented in Table 1. Direct crystallization of host **3** from TCE yielded crystals of $(\mathbf{3})_2\cdot$(TCE) in the triclinic space group P-1. Molecular structure of $(\mathbf{3})_2\cdot$(TCE), including thermal displacement ellipses with 50% probability, is illustrated in Fig. 1.

Presence of four heteroatoms, nitrogen, sulfur, bromine, and chlorine, increases the possible supramolecular motifs, which exist in the crystal structure of the resulted lattice inclusion compound. These motifs would be in terms of host–host, host–guest, and guest–guest interactions to produce the best fit crystal packing. Molecules of opposite chirality of host **3** form infinite chains through a new type of aromatic edge–edge interaction that produce two different centrosymmetric aryl C-Br···N dimer interactions (Br···N 3.60 and 3.63 Å). As illustrated in Fig. 2., short Br···Br contact (3.59 and 3.54 Å) across the middle of each of these edge–edge motifs was observed to form two fused five-membered rings.

Longer Br···Br interactions are observed between molecules of host **3** with contact distances of 3.99 Å and 3.84 Å; in addition the Br···H interaction is linked between molecules of **3** of opposite chirality with contact distances of 3.11 Å and 2.96 Å as shown in Figs. 3 and 4.

Replacement of the bridging methylene group by a sulfur atom resulted in a great change in the supramolecularity of the resulted crystal structure. Sulfur atom of the host molecule **3** interacts with the bromine atom of another host molecule with a contact distance of 3.62 Å to produce a new centrosymmetric dimer as shown in Fig. 5.

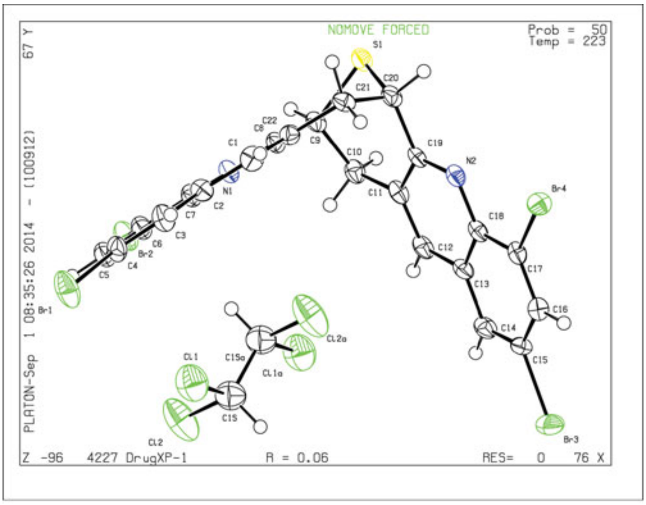


Figure 1. Thermal ellipsoid plot of $(\mathbf{3})_2\cdot$(TCE) lattice inclusion compound drawn at 50% probability.

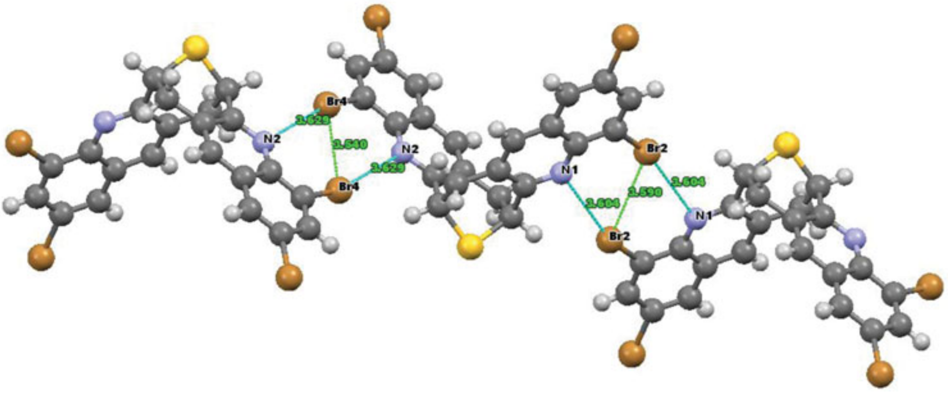


Figure 2. Opposite enantiomers of host **3** alternate along the chain and linked by two different centrosymmetric aryl C-Br···N dimer interactions.

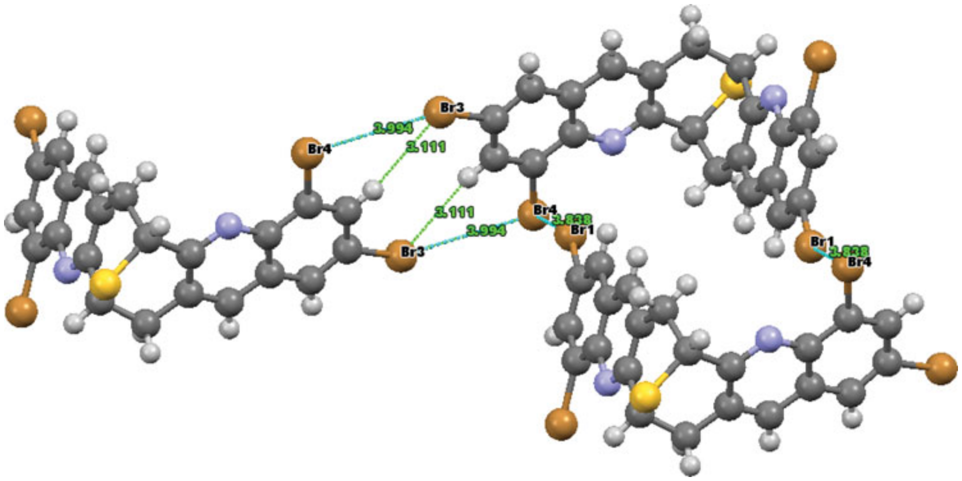


Figure 3. Opposite enantiomers of host **3** alternate along the chain and linked by three different centrosymmetric aryl Br···Br and Br···H dimer interactions.

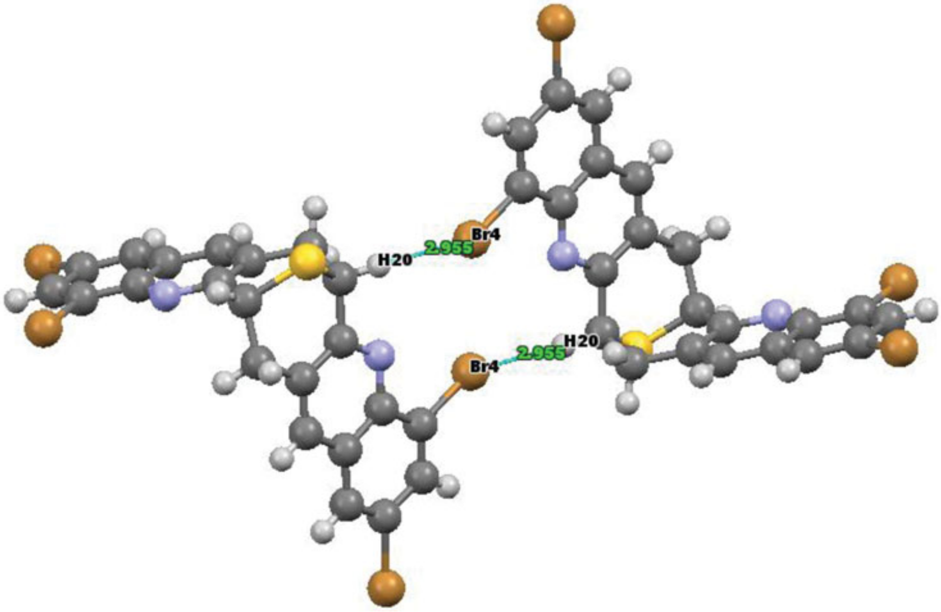


Figure 4. Another type of Br···H motif exists in the crystal structure of **3** and produced different centrosymmetric Br···H dimer interactions.

Sulfur···hydrogen interaction plays an important role in linking molecules of host **3** by forming a centrosymmetric tetramer with a distances of 3.43 Å and 3.67 Å as illustrated in Fig. 6.

Host–guest interactions were observed in the crystal structure of (**3**)$_2$·(TCE) lattice inclusion compound. One guest molecule is interacting with two host molecules of opposite chirality to form such molecular pen. Different motifs of interactions exist between host and guest molecules of this molecular pen, such as N···H (3.13 Å), N···Cl (4.14 Å), and Cl···Br (3.87 Å) as shown in Fig. 7.

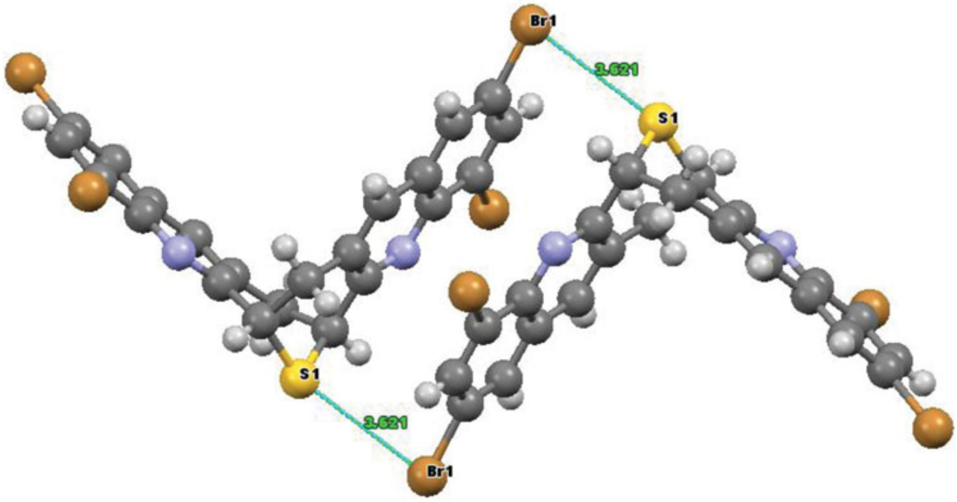


Figure 5. Sulfur atom of one host molecule **3** is interacting with bromine atom of another host molecule to produce a centrosymmetric dimer.

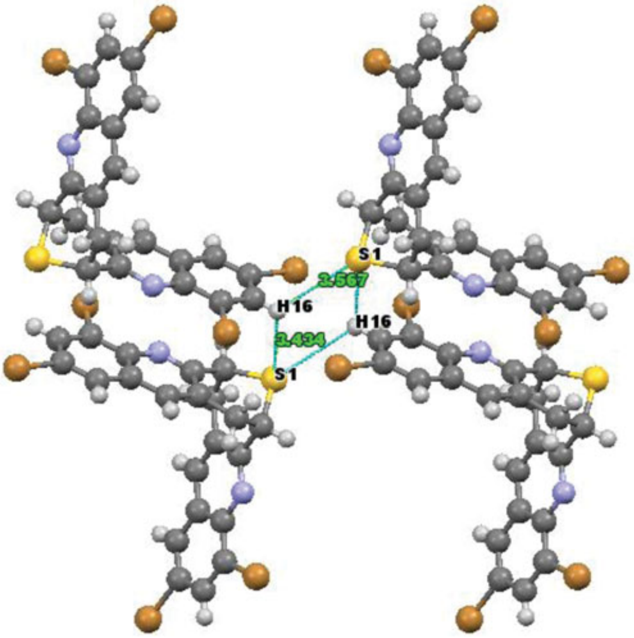


Figure 6. Molecules of host **3** interacting through S⋯H motif to produce a centrosymmetric tetramer.

Part of a layer present in the $(\mathbf{3})_2\cdot$(TCE) structure, showing how the TCE guest molecules are enclosed in molecular pens, is presented in Fig. 8. The molecular pens are linked by a centrosymmetric arrangements of Br⋯N interactions. All the halogen bonding interactions are weak. The C-Br⋯Br-C interaction is a dominant type of halogen bonding. In the crystal

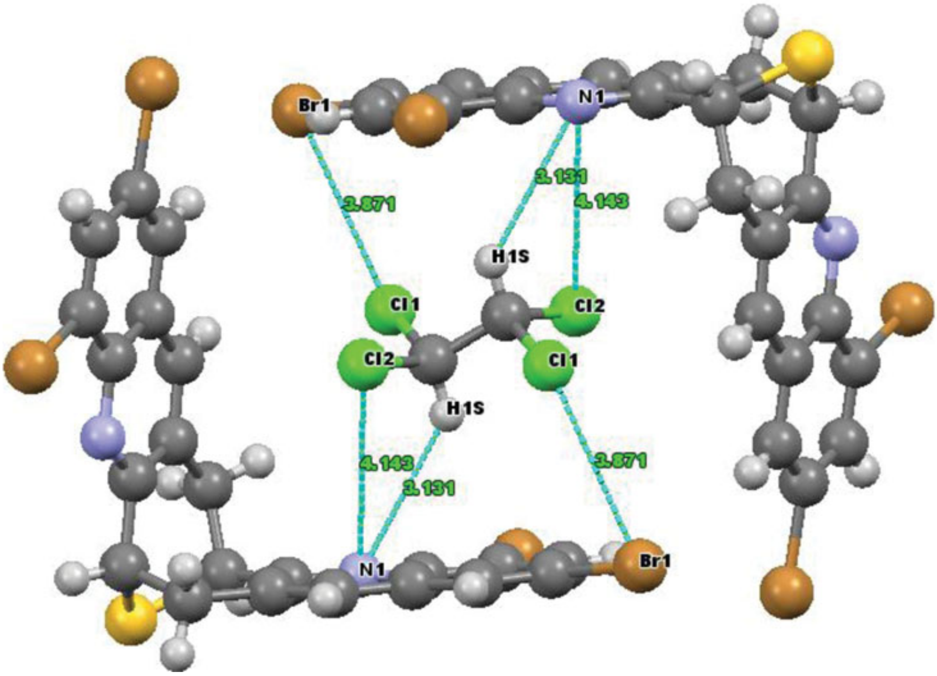


Figure 7. Different motifs of host–guest interactions existing in compound **3**.

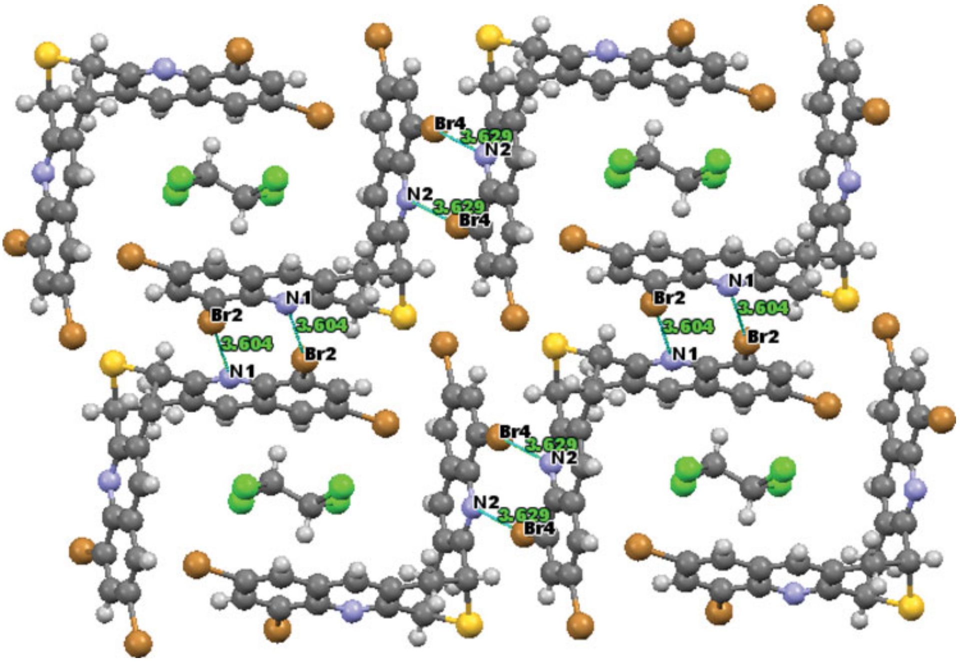


Figure 8. Part of layer of molecular pens in the structure of $(\mathbf{3})_2\cdot$(TCE) linked together by centrosymmetric Br···N interactions.

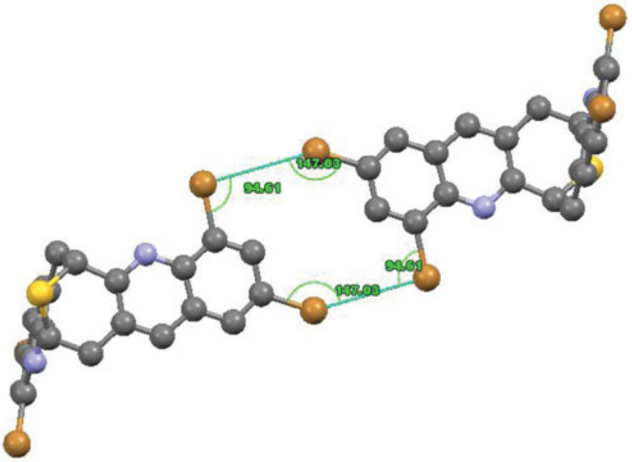
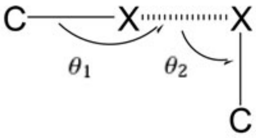


Figure 9. The C-Br···Br-C bond angles exist in the crystal structure of $(\mathbf{3})_2\cdot$(TCE), where $\theta_1 = 147.03^\circ$ and $\theta_2 = 94.61^\circ$.

structure of $(\mathbf{3})_2\cdot$(TCE), it was very interesting to observe that bromine atoms of different host molecules play an important role in the packing of host molecules. Host molecules are interacting together to form zigzag chains with an orientation that Desiraju [19–21] defined as type II orientation (Chart 1), where $\theta_1 = 147.03^\circ$ and $\theta_2 = 94.61^\circ$ (Fig. 9). The halogen …nitrogen and halogen …halogen contact distances are in good agreement with what we have observed and reported in some related systems [7,22,23].



Type II [$\theta_1 \approx 180^\circ$; $\theta_2 \approx 90^\circ$]

Chart 1

Conclusions

Host molecules of 2,4,10,12-tetrabromo-6,7,14,15-tetrahydro-6,14-thiacyclo-octa[1,2-b:5,6-b']diquinoline were re-synthesized, and were able to form a stable lattice inclusion compound with toxic TCE. The X-ray crystal structure of the resulted lattice inclusion compound is described and analyzed in terms of crystal engineering and supramolecular chemistry. The hosts assemble by means of different types of packing motifs, and form molecular pen structure in which the included TCE molecules are enclosed. Novel halogen⋯halogen intermolecular interactions as well as other non-covalent intermolecular interactions involved in the crystal structure are presented and proved to play an important role in linking these host–host, host–guest, and guest–guest building blocks.

Acknowledgments

The author would like to thank Mutah University and National University of Singapore for technical support and assistance needed to finish and obtain this work in its current form.

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