
**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Xu, Jianwei , Wang, Wei-Ling , Lin, Tingting , Sun, Zhe and Lai, Yee-Hing(2008) 'Molecular assembly of dithiaparacyclophanes mediated by non-covalent X...X, X...Y and C-H...X (X, Y=Br, S, N) interactions', Supramolecular Chemistry, 20: 8, 723 — 730
**To link to this Article: DOI:** 10.1080/10610270701787723
**URL:** http://dx.doi.org/10.1080/10610270701787723

*Supramolecular Chemistry*
Vol. 20, No. 8, December 2008, 723–730

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# Molecular assembly of dithiaparacyclophanes mediated by non-covalent X···X, X···Y and C—H···X (X, Y = Br, S, N) interactions

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(*Received 7 August 2007; final version received 1 November 2007*)

Regioselectivity for the 5,8,15,18-substituted isomer over the 5,8,14,17-isomer was observed in a series of mercaptan–bromide coupling reactions leading to the formation of 2,11-dithia[3.3]paracyclophanes. Their molecular assembly was established by X-ray crystallographic studies. In the crystal packing of these paracyclophanes, several types of non-covalent interactions including halogen–halogen interaction, halogen-bonding interaction, weak hydrogen-bonding interaction, etc. are observed in crystals **3a**, **3b** and **3c**. There is evidence to indicate that weak non-covalent Br···Br, Br···S, Br···N, C—H···S, S···S and C—H···N interactions play an important role in governing their molecular assembly assumed in the solid state. The attractive interactions of Br···Br, Br···S and Br···N are also rationalised and supported in terms of the density functional theory calculations.

**Keywords:** molecular assembly; dithiaparacyclophanes; halogen bonding; bromine–bromine interaction



## 1. Introduction

Weak intermolecular interactions, particularly hydrogen-bonding interaction play a vital role in molecular recognition, conformational transformation and molecular assembly (*1*). Numerous examples are also reported that hydrogen bonding is a driving force to induce the formation of supramolecular liquid crystals (*2–6*). Like hydrogen bonding, halogen bonding is known as the interaction between Z—X···Y, where X is a halogen atom and acts as an electron acceptor and Y is an electron-negative atom (e.g. N, O and S) and functions as an electron donor. It exhibits remarkable similarity with hydrogen bonding in many aspects. For example, halogen bonding effectively enhances the linear molecular assembly especially between perfluoroalkane halides and nitrogen-containing organic molecules (*7–11*), and induces the formation of liquid crystals (*12–15*). Halogen–halogen interaction (for example, C—X···X—C) is however, another type of weak interaction involved in halogens, which is ever considered as 'donor–acceptor' interaction, 'secondary' interaction, 'electron-transfer' and 'highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)' interaction (*16–19*). Either halogen bonding or halogen–halogen interactions could be found in many halogen-containing organic crystals and are believed to be an attraction force to stabilise crystals (*20–25*).

Halogen-bonded supramolecular molecular assemblies are usually formed by linear or planar molecules via single halogen-bonding association, but few are found to be involved in non-planar layered molecules like cyclophanes. Recently, our work has been directed towards the synthesis of selectively halogen-substituted dithia[3.3]paracyclophanes and their corresponding [2.2]paracyclophanes as building blocks to functional polymers (*26–29*). It is of interest to explore the role of weak non-covalent interactions such as halogen bonding and halogen–halogen interaction in the molecular assembly of halogen-substituted dithia[3.3]paracyclophane. In addition, dithia[3.3]paracyclophanes are important precursors to [2.2]paracyclophanes (*30–32*) and have been employed as building blocks in integrating supramolecular assembly with transition metal ions (*33–35*). The preparation of dithiacyclophanes by a bromide–mercaptan cyclisation under high dilution conditions is well known (*36–38*). The stereochemical preference of such reactions to form multisubstituted dithia[3.3]paracyclophanes, however, has not been studied systematically. In this paper, we report on the regioselectivity in the synthesis of a series of multi-substituted dithia[3.3]paracyclophanes **3**. Their structures are confirmed by spectroscopic methods and X-ray crystallography. Most importantly, X-ray crystallographic analysis of **3a**, **3b** and **3c** shows the presence of multiple non-covalent interaction, revealing that weak Br···Br, Br···S, Br···N, S···S, C—H···N and C—H···S interactions are likely to play an important role in the

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ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610270701787723
http://www.informaworld.com

molecular assembly of these non-planar layered halogenated paracyclophanes in the solid state.

## 2. Experimental section

### 2.1 Instrumentation

All reactions were carried out under nitrogen. Commercially available reagents and solvents were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker ACF300 spectrometer in $CDCl_3$. Electron impact mass spectroscopy (EIMS) and fast atom bombardment mass spectroscopy (FAB-MS) spectra were recorded using a Micromass 7034E mass spectrometer. Elemental analysis was conducted on a Perkin–Elmer 240C elemental analyser for C, H and S determination at the Chemical and Molecular Analysis Centre, Department of Chemistry, National University of Singapore. The data were measured on a Siemens SMART 3-circle diffractometer with a charge-coupled device (CCD) area detector using graphite-monochromated Mo $K_\alpha$ radiation and equipped with an Oxford Cryosystems cryostream. The structures were solved by direct method, and refinement, based on $F^2$ of all data, was by full-matrix least-squares techniques, using SHELX-97. The structures were solved by direct methods with any remaining non-hydrogen atoms located from different Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters. Refinements were made by full-matrix least-squares methods and final refinements were made on $F^2$ using a weighting scheme of the form $w = 1/[\sigma^2(F_0^2 + (aP)^2 + bP)$, where $P = [\max(F_0^2) + 2(F_c^2)]/3$.

### 2.2 Materials

#### 2.2.1 General procedure for the synthesis of tetrasubstituted dithia[3.3]paracyclophanes

A solution of **1** (3.0 mmol) and **2** (3.0 mmol) in degassed benzene was added dropwise with vigorous stirring to a solution of KOH (6.0 mmol) in 95% ethanol (1 l). After the addition was completed, the reaction mixture was stirred for an additional 20 h at room temperature. The solvent was then removed under reduced pressure and the crude product was dissolved in dichloromethane. The organic solution was washed with water, dried and filtered. The solvent was removed and the residue chromatographed on silica gel to afford a mixture of **3** and **4** as white solids. Recrystallisation of the mixture of **3** and **4** in benzene or toluene gave pure **3**. The molar ratio of isomers **3** and **4** in the reaction mixture was estimated by comparing the integration area of corresponding cyclophane bridge hydrogen signals of **3** and **4** in the $^1$H NMR spectra.

#### 2.2.2 5,8-Dibromo-2,11-dithia[3.3]paracyclophane (**3a**)

Yield: 60%; mp 239–241°C; $^1$H NMR ($CDCl_3$): $\delta$ 3.62 (d, $J = 15.1$ Hz, 2H), 3.80 (d, $J = 15.1$ Hz, 2H), 3.89 (d, $J = 15.1$ Hz, 2H), 4.15 (d, $J = 15.1$ Hz, 2H), 7.02 (d, $J = 9.4$ Hz, 2H), 7.17(d, $J = 9.4$ Hz, 2H), 7.18 (s, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ 36.57, 37.76, 123.31, 128.08, 129.37, 135.15, 135.24, 136.85; MS (*m*/*z*): 430 ($M^+$); calcd for $C_{16}H_{14}Br_2S_2$: C, 44.67; H, 3.28; found: C, 44.69; H, 3.17.

#### 2.2.3 5,8,15,18-Tetrabromo-2,11-dithia[3.3]paracyclophane (**3b**)

Yield: 55%; mp 256–259°C; $^1$H NMR ($CDCl_3$): $\delta$ 3.68 (d, 4H, $J = 15.1$ Hz), 3.95 (d, 4H, $J = 15.1$ Hz), 7.47 (s, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 37.05, 123.65, 134.21, 136.33; MS (*m*/*z*) 584 ($M^+$); calcd for $C_{16}H_{12}Br_4S_2$: C, 32.68; H, 2.06; found: C, 32.51; H, 1.93.

#### 2.2.4 5,8-Dibromo-15,18-dicyano-2,11-dithia[3.3]paracyclophane (**3c**)

Yield: 65%; mp >300°C; $^1$H NMR ($CDCl_3$): $\delta$ 3.77 (d, 2H, $J = 15.2$ Hz), 3.86 (d, 2H, $J = 15.5$ Hz), 3.99 (d, 2H, $J = 15.2$ Hz), 4.09 (d, 2H, $J = 15.5$ Hz), 7.42 (s, 2H), 7.75 (s, 2H); $^{13}$C NMR ($CDCl_3$) 35.00, 37.08, 115.63, 116.85, 123.72, 133.56, 135.12, 136.55, 140.29; MS (*m*/*z*) 480 ($M^+$); calcd for $C_{18}H_{12}Br_2N_2S_2$: C, 45.02; H, 2.52; N, 5.83; found: C, 45.20; H, 2.61; N, 5.90.

#### 2.2.5 5,8,-Dibromo-15,18-diphenyl-2,11-dithia[3.3]paracyclophane (**3d**)

Yield: 37%; mp 225–229°C; $^1$H NMR ($CDCl_3$): $\delta$ 3.49 (d, 2H, $J = 14.8$ Hz), 3.86 (d, 2H, $J = 15.7$ Hz), 4.03 (d, 2H, $J = 14.8$ Hz), 4.12 (d, 2H, $J = 15.7$ Hz), 7.16 (s, 2H), 7.37–7.66 (m, 12H); $^{13}$C NMR ($CDCl_3$) 36.24, 37.75, 122.96, 127.10, 128.51, 129.05, 131.58, 133.02, 133.88, 137.18, 139.95, 140.64; MS (*m*/*z*) 582 ($M^+$); calcd for $C_{28}H_{22}Br_2S_2$: C, 57.74; H, 3.81; found: C, 58.01; H, 3.89.

#### 2.2.6 5,8,-Dimethoxy-15,18-diphenyl-2,11-dithia[3.3]paracyclophane (**3e**)

Yield: 33%; mp 230–232°C; $^1$H NMR ($CDCl_3$): $\delta$ 3.35 (d, 2H, $J = 14.1$ Hz), 3.81 (s, 6H), 3.87 (d, 2H, $J = 15.0$ Hz), 4.01 (d, 2H, $J = 14.1$ Hz), 4.06 (d, 2H, $J = 15.0$ Hz), 6.46 (s, 2H), 7.35–7.63 (m, 12H); $^{13}$C NMR ($CDCl_3$) 32.31, 36.09, 57.88, 115.76, 126.45, 126.93, 128.34, 129.12, 131.93, 133.09, 139.35, 140.81, 151.34; MS (*m*/*z*) 484; calcd $C_{30}H_{28}O_2S_2$: C, 74.34; H, 5.82; found: C, 74.56; H, 6.05.

Table 1. Summary of crystallographic data for compounds **3a**, **3b** and **3c**.

| | **3a** | **3b** | **3c** |
|---|---|---|---|
| Empirical formula | $C_{16}H_{14}Br_2S_2$ | $C_{16}H_{12}Br_4S_2$ | $C_{18}H_{12}Br_2N_2S_2$ |
| Formula weight | 430.21 | 588.02 | 480.24 |
| Crystal colour | Colourless | Colourless | Colourless |
| Crystal size | 0.34 × 0.10 × 0.06 | 0.30 × 0.13 × 0.13 | 0.46 × 0.10 × 0.09 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P-1$ | $Cc$ | $P2_1c$ |
| $a$ (Å) | 6.9563(6) | 9.1102(5) | 17.5997(11) |
| $b$ (Å) | 10.0455 (9) | 15.1617 (9) | 6.8768(4) |
| $c$ (Å) | 12.1488 (10) | 12.7480(8) | 29.8669 (17) |
| $\alpha$ (°) | 104.573 (2) | 90 | 90 |
| $\beta$ (°) | 102.364 (2) | 95.0250 (10) | 98.199 (2) |
| $\gamma$ (°) | 104.102 (2) | 90 | 90 |
| $V$ (Å$^3$) | 761.80 (11) | 1754.1(2) | 3577.8(4) |
| $Z$ | 2 | 4 | 8 |
| $D_c$ (Mgm$^{-3}$) | 1.876 | 2.227 | 1.783 |
| $T$ (K) | 298.15 | 298.15 | 298.15 |
| $\mu$(Mo K$_\alpha$) (mm$^{-1}$) | 5.581 | 9.408 | 4.767 |
| $\theta$ range (for data collection) | 1.81–29.95° | 2.62–29.38° | 1.67–27.50° |
| $F$(000) | 424 | 1120 | 1888 |
| GOF | 1.048 | 1.031 | 0.939 |
| $R_1$ (for $I > 2\sigma(I)$) | 0.05269 | 0.0292 | 0.0527 |
| $wR_2$ (for all data) | 0.0736 | 0.0691 | 0.1228 |

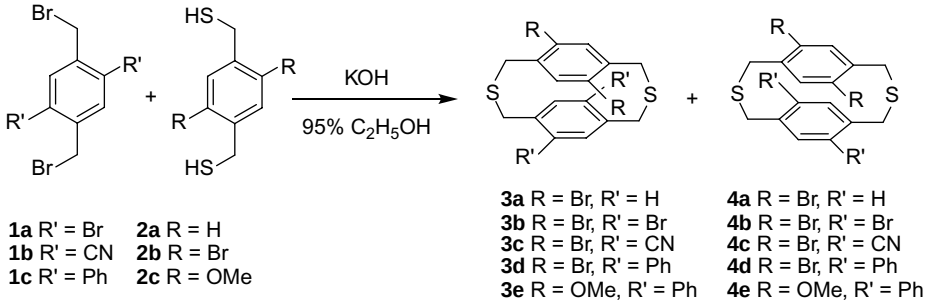


#### 2.2.7 *Crystallographic data for compounds **3a**, **3b** and **3c** are summarised in Table 1*

The molecular structures were optimised using the density functional theory (DFT) electronic structure program DMol[3] available as part of Materials Studio (Accelrys Inc.). In this code, the electronic wave function was expanded in a localised atom-centred basis set with each basis function defined numerically on a dense radial grid. All electron calculations were performed with a double numeric polarised basis set (which is analogous to the Gaussian 6-31(d,p) basis set), the most complete set available in the code. The gradient-corrected Becke-Lee-Yang-Parr (density functional theory) (BLYP) functional, a finite basis-set cut-off of 4.0 Å and a 'fine' quality (convergence tolerances: energy $1.0 \times 10^{-5}$ Ha, maximum force 0.002 Ha/Å, maximum displacement 0.005 Å; self-consistent-field (SCF) tolerance $1.0 \times 10^{-6}$) were used.

## 3. Results and discussion

The synthetic route leading to the series of dithia[3.3]-paracyclophanes is shown in Scheme 1. Compounds **1a**, **1b** and **1c** were readily prepared by bromination of their corresponding 2,5-disubstituted-1,4-dimethylbenzene. Reaction of **1a** or 1,4-bis(bromomethyl)-2,5-dimethoxybenzene with thiourea, followed by hydrolysis in aqueous $Na_2CO_3$ gave **2a** or **2b**, respectively. A high dilution coupling reaction (*36–42*) of **1** and **2** was carried out in a mixture of benzene and ethanol in the presence of KOH at room temperature. The corresponding tetrasubstituted dithia[3.3]paracyclophanes were isolated after column chromatography and recrystallisation. Both the 5,8,15,18-isomer **3** and its 5,8,14,17-isomer **4** could be formed in the coupling reaction. Qualitatively, a preference for **3** is expected on the basis of their relative steric energies, where transannular eclipsed interactions




**1a** R' = Br **2a** R = H
**1b** R' = CN **2b** R = Br
**1c** R' = Ph **2c** R = OMe

**3a** R = Br, R' = H **4a** R = Br, R' = H
**3b** R = Br, R' = Br **4b** R = Br, R' = Br
**3c** R = Br, R' = CN **4c** R = Br, R' = CN
**3d** R = Br, R' = Ph **4d** R = Br, R' = Ph
**3e** R = OMe, R' = Ph **4e** R = OMe, R' = Ph

Scheme 1. Synthesis of paracyclophanes **3** and **4**.

in **4** is expected to be less favourable. Experimentally, isomer **3** was isolated as a main product irrespective of the electronic and/or the steric nature of the substituents. In fact, the molar ratios between **3** and **4** were estimated by the integration of their $^1$H NMR signals to be 40:1, 20:1, 50:1 and 35:1 for **3b**:**4b**, **3b**:**4b**, **3d**:**4d** and **3e**:**4e**, respectively. The structures of **3a**–**3e** are supported by spectroscopic studies. In the $^1$H NMR spectrum of **3b**, the diastereotopic benzylic protons appear as an AB quartet at $\delta$ 3.68 and 3.95, and the aromatic protons as a singlet at $\delta$ 7.47. In its $^{13}$C NMR spectrum, four signals observed at $\delta$ 37.05, 123.65, 134.21 and 136.33 are in accordance with the structure of **3b**. The two kinds of non-equivalent benzylic protons in **3c**–**3e** appear as two separate sets of AB quartets in their $^1$H NMR spectra. Their benzylic carbons are also resolved into two signals in the range of $\delta$ 32–38 in the $^{13}$C NMR spectra. All compounds **3a**–**3e** show their molecular ions in their respective mass spectra. However, the above data could not rule out the structures **4b**–**4e** affirmatively. The absolute structures of **3a**, **3b** and **3c** were eventually determined by X-ray crystallography. Single crystals of **3b** and **3c** were grown from their benzene and toluene solutions, respectively. The X-ray crystal structural analysis thus confirms the structures of **3a**, **3b** and **3c** and indirectly those of **3d** and **3e**.

It is interesting to note that the sulphur bridges in **3a** assume a pseudochair conformation while those in **3b** (and **3c**) adopt a pseudoboat stereochemistry. The interplanar distances of the two aromatic rings in **3a**, **3b** and **3c**, ranging from 3.264 to 3.301 Å, are shorter than that of the normal packing distance of aromatic rings in organic molecules (3.4 Å), suggesting probable transannular $\pi-\pi$ interactions. For all three cyclophanes, the aromatic rings do not deviate significantly from planarity (mean deviation $<0.03$ Å), but form a very small inter-ring angle of 1.2, 1.2/0.4,[2] and 1.1°, respectively for **3a**, **3b** and **3c**.

Compounds **3a**, **3b** and **3c** crystallise in the space group $P-1$, $Cc$ and $P2_1c$, respectively. The crystal packings of paracyclophanes **3a**, **3b** and **3c** are shown in Figures 1–3, respectively. Although, the bridges in **3a** and **3b** take on different conformations, both their crystal packings are indicative of various interesting weak interactions. Intermolecular contacts and angles of C—X···Y (X, Y = Br, S, N) and C—H···X (X = S, N) in **3a**, **3b** and **3c** are summarised in Table 2. In **3a**, each of the two bromine atoms is in close proximity to a bridge sulphur atom in any two adjacent cyclophane units (Br···S = 3.543 and 3.614 Å; Figure 1). One of the sulphur atoms in turn interacts with one of the benzylic hydrogen atoms (S···H = 2.947 Å). In **3b**, both Br···S and Br···Br

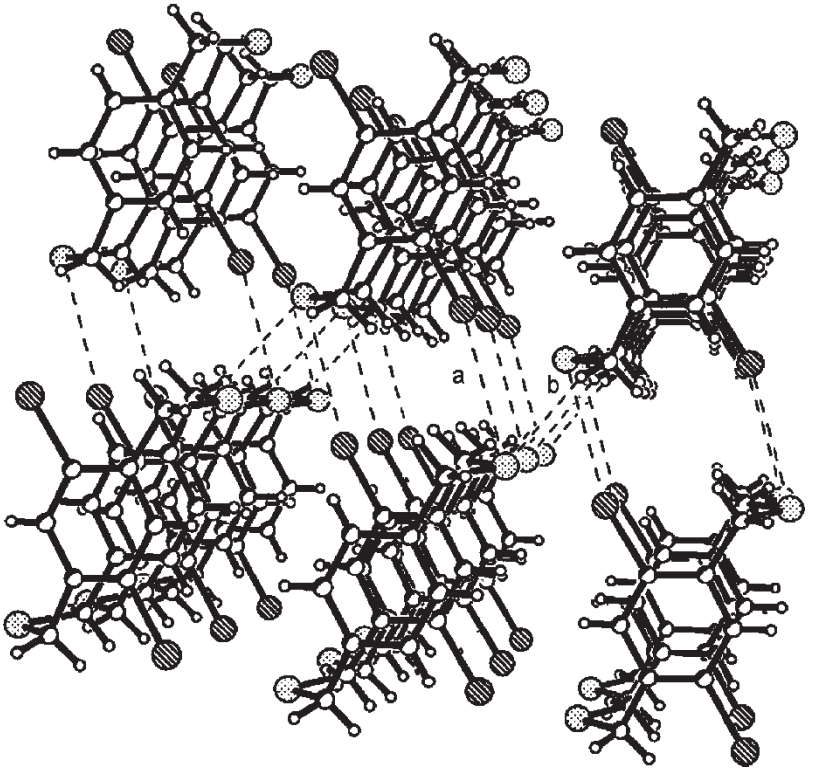



Figure 1. Crystal packing of **3a**. The dashed lines represent the atom–atom interactions: (a) bromine–sulphur and (b) sulphur–hydrogen.

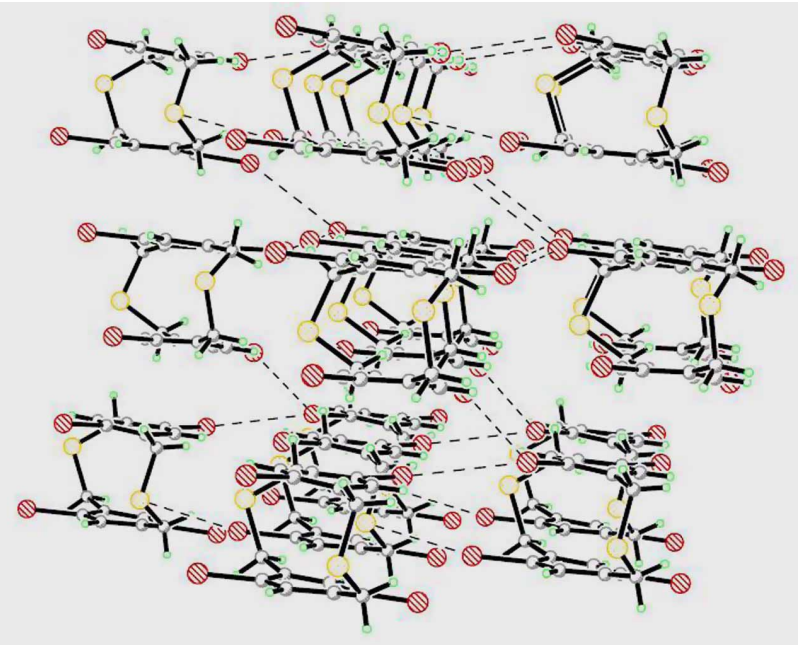


Figure 2. Crystal packing of **3b**. The dashed lines represent the atom–atom interactions: (a) bromine–sulphur; (b and c) bromine–bromine.



contacts are observed. One of the bromine atoms in each cyclophane interacts with two bromine atoms from two independent cyclophanes (Br···Br = 3.788 and 3.831 Å;

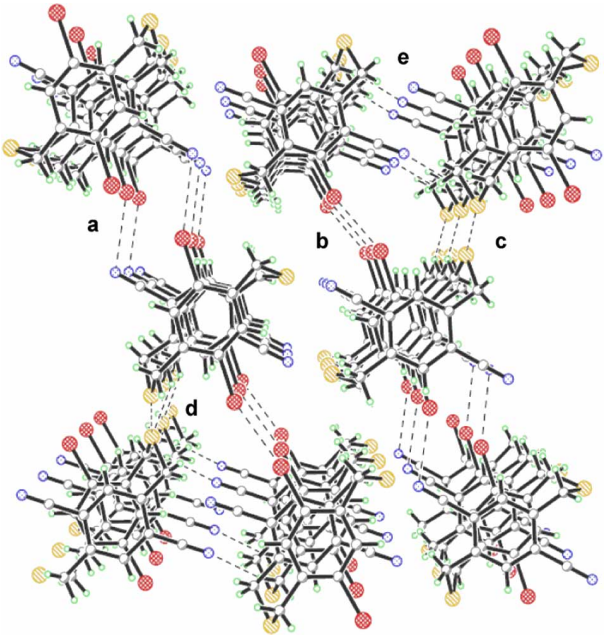



Figure 3. Crystal packing of **3c**. The dashed lines represent the atom–atom interactions: (a) bromine–nitrogen; (b) bromine–bromine; (c) sulphur–sulphur; (d) sulphur–hydrogen; (e) nitrogen–hydrogen.

Figure 2). Two conformers are observed in the **3b** crystal, one of which is located in the adjacent layer. The distances of the Br···Br are slightly longer than the van der Waals diameter of bromine (3.72 Å). On the contrary, the Br···S distances (3.534, 3.614 and 3.609 Å) in both **3a** and **3b** are shorter than the sum of van der Waals radii of bromine and sulphur atoms (3.71 Å; (*43*)). In **3c**, there is intermolecular Br···N contact as well as C—H···S, Br···Br, C—H···N and C—S···S contacts (Figure 3). Except for the distances between the Br···Br (3.834 Å) contact, the distances of the Br···N (3.258 Å), S···S (3.345 Å), S···H (2.866 Å) and N···H (2.49 Å) are shorter than those of their corresponding sum of van der Waals radii (*43*) (3.36, 3.72, 3.05 and 2.70 Å, respectively, for Br···N, S···S, S···H and N···H) by 3–10%. Similarly, all of the Br···S and the Br···N distances in **3b** and **3c** are also shorter than the corresponding sum of van der Waals radii.

In all such close contacts in **3a**, **3b** and **3c**, the C—H···N contact was verified to be a type of weak hydrogen bonding (*1, 44, 45*). A large number of examples have showed there are the close contacts of C—H···N, which stabilises the crystal packing. Apart from hydrogen bonding, the importance of other non-covalent weak interactions such as Br···Br (*43, 46–48*), Br···S (*49*), Br···N (*49, 50*), etc. interactions are increasingly recognised to play a key role in the molecular assembly of many systems. The non-bonded C—H···S contacts in **3a** and **3c** are expected to be a weaker interaction than the C—H···N interaction due to

Table 2. Intermolecular contacts (Å) and angles (°) of C—X···Y (X, Y = Br, S, N) and C—H···X (X = S, N) in **3a**, **3b** and **3c**.

| Intermolecular contact (Å) | **3a** | **3b** | **3c** | Sum of van der Waals radii (Å)[a] | Angle (°) | **3a** | **3b** | **3c** |
|---|---|---|---|---|---|---|---|---|
| Br···Br | | 3.831(6) | 3.834(6) | 3.72 | C—Br···Br | | 121.1(5), 123.2(4) | 136.5(3), 133.2(4) |
| | | 3.788(4) | | | | | 148.9(2), 151.8(3) | |
| Br···S | 3.614(3) | 3.609(4) | | 3.71 | C—Br···S | 162.7(2) | 153.5(7) | |
| | 3.534(4) | | | | | 162.7(6) | | |
| Br···N | | | 3.258(3) | 3.36 | C—Br···N | | | 153.0(7) |
| S···H | 2.947(5) | | 2.866(5) | 3.05 | C—H···S | 158.0(5) | | 150.7(5) |
| N···H | | | 2.49(2) | 2.70 | C—H···N | | | 167.7(4) |
| S···S | | | 3.345(4) | 3.70 | C—S···S | | | 171.9(4), 84.8(3); 170.9(5), 82.5(4) |

[a]The sum of van der Waals radii is estimated according to the following atomic radii: rS: 1.85 Å; rH: 1.20 Å; rBr: 1.86 Å and rN: 1.50 Å.

the fact that nitrogen has a larger electronegativity than sulphur. The calculation showed that the C—H···S interaction energy in the $H_3C$—H···$SH_2$ complex was estimated to be $-0.84\,kcal\,mol^{-1}$ (*51*). On the other hand, the S···S contacts in organic crystals or organometallic complexes are not rare (*52–56*), and a majority of these contacts correspond to an attractive electrophile–nucleophile paring and contribute to HOMO–LUMO interaction, depending on the mutual approach directions of two sulphur atoms (*52*). In the case of crystals, **3a**, **3b** and **3c**, the C—H···S or S···S interactions should cooperate with other interactions observed and make contribution to the stabilisation of crystal packing. Previously, we have reported an analogous example of a supramolecular assembly of a crownophane–$Na^+$ complex stabilised by the C—H···S interactions (*57*).

In **3b** and **3c**, the distance between two bromine atoms, from 3.788 to 3.834 Å, is just above the sum of van der Waals radii of two bromine atoms, and this type of interaction is mainly interpreted as the dispersion force (*19*). In general, halogen–halogen contacts have two preferred geometries: $\theta1 = \theta2$ (type I) or $\theta1 = 90°$ and $\theta2 = 180°$ (type II), where $\theta1$ and $\theta2$ present the two C—X···X angles (*19*). The geometries for all Br···Br contacts observed in crystals **3a** and **3b** correspond to type I (Table 2). In contrast, the distances for halogen bonding Br···S and Br···N in compounds **3a**, **3b** and **3c** are less than the corresponding sum of van der Waals radii and the angles for C—Br···S and C—Br···N vary in the range of 153–163°. The most interesting observations of this study is that the structures of compounds **3a**, **3b** and **3c** form a network in which molecules are linked via either halogen bonding Br···S or Br···N together with other weak interactions C—H···S, Br···Br, C—H···N and even S···S interactions. The angular geometries of these interactions and intermolecular contact distances are basically in agreement with the preferred values. These findings indicate that these weak interactions serve an important role and cooperatively stabilise the crystal packing.

To explore the nature of these close contacts in the substituted dithia[3.3]paracyclophane studied in our present work, DFT calculations were carried out employing three model compounds, dithia[3.3]paracyclophane, bromobenzene and cyanobenzene. Three interaction models I (dithia[3.3]paracyclophane and bromobenzene for Br···S), II (cyanobenzene and bromobenzene for Br···N) and III (bromobenzene and bromobenzene for Br···Br) as illustrated in Figure 4 are selected to estimate the stabilisation energy (Es). The energy at which the two molecules are located at infinite separation is chosen as the reference level. The calculated stabilisation energy for the three interactions is indeed estimated to be attractive in nature (Table 3).

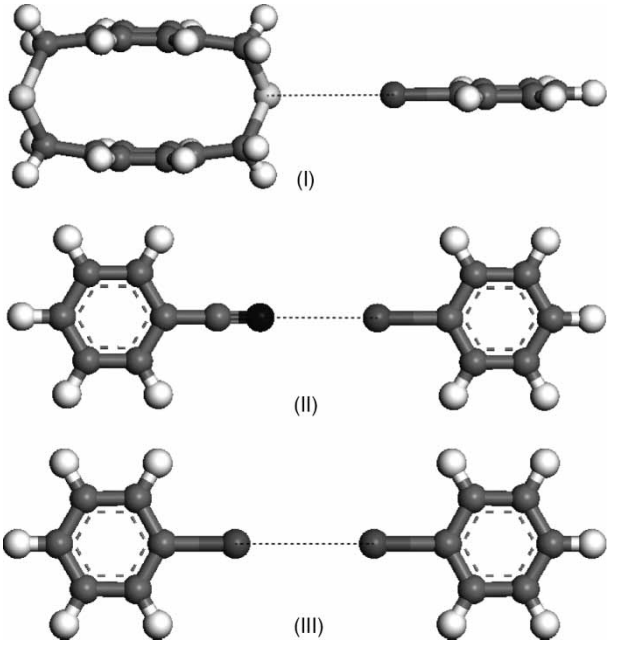



Figure 4. Interaction models of Br···S (I), Br···N (II) and Br···Br (III) used for DFT calculations.

Table 3. The calculated stabilisation energy by DFT method.

| Interaction | Es (kcal mol$^{-1}$) | Interaction | Es (kcal mol$^{-1}$) |
|---|---|---|---|
| C—Br···S | −2.78 | C—Br···N | −2.31 |
| C—Br···Br | −1.36 | | |

## 4. Conclusions

Weak interactions (C—X···Y, where X = halogen and Y = halogen or sulphur, or X = hydrogen and Y = sulphur or nitrogen) were reported to serve as a driving force for the supramolecular assembly in several systems (*58, 59*). The close contacts in the cyclophanes **3a**, **3b** and **3c** are thus believed to be a consequence of the specific attractions stabilising the molecular assembly instead of a physical outcome of crystal packing. Such contacts may render unique geometries in the molecular assembly of the stacked or layered molecules like paracyclophanes. This information may be at large of value to the design, prediction and understanding of molecular assembly of the oligomers and polymers derived from these cyclophanes.

## Supporting information available

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC-194200 (**3a**), CCDC-189356 (**3b**) and CCDC-194201 (**3c**).

## Acknowledgements

This work was supported by the National University of Singapore (NUS) and Institute of Materials Research and Engineering (IMRE). We are grateful to Associate Professor J.J. Vittal and Ms Tan Geok Kheng of the Chemical and Molecular Analysis Centre, Department of Chemistry, NUS for their assistance in X-ray crystallographic determination.

## Notes

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2. Two conformers were observed in the crystal of **3b**.

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