Molecular Tectonics. Use of Br $\cdots$ aryl Supramolecular Interactions for the construction of Organized Networks from 9,9'-spirobifluorene in the Crystalline State.

Ulrich Darbost^{1*}, Janie Cabana², Eric Demers², Thierry Maris^{2*} and James D. Wuest^{2*}

¹Université de Lyon, Lyon, Université Lyon 1, Villeurbanne, CNRS, UMR 5246, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Equipe CSAp, 43 Boulevard du 11 Novembre 1918, F-69622, Villeurbanne, France.

²Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7 Canada

Tel: 1-514-340-5178, E-mail: james.d.wuest@umontreal.ca

doi:10.5618/chem.2011.v1.n1.7 || Received: 29-07-2011, Accepted: 15-09-2011, Available online: 29-10-2011

Abstract

Numerous studies, many based on statistical analyses of structural data from the Cambridge Structural Database (CSD), have highlighted the importance of halogen $\cdots$ aryl interactions. Although the exact value of the binding energy is still a subject of debate, it is generally agreed that such interactions can play an important role in crystal packing. For example, previous work by Desiraju and collaborators has shown that Br $\cdots$ aryl interactions generate characteristic supramolecular motifs, which may be useful for designing molecular solids [2].

With this goal in mind, we set out to use 9,9'-spirobifluorene (SBF) or tetrabrominated SBF derivatives as tectons [3] and to see if Br $\cdots$ aryl interactions can be used to build predictable molecular networks. Several features made the SBF core an attractive candidate for this study: 1) SBF has D_{2d} symmetry, is rigid and orients its aromatic rings and their substituents in distinct directions of space; 2) the synthesis of SBF derivatives has been described; and 3) derivatives of SBF tend to crystallize readily, frequently as inclusion complexes, which allows the study of interactions between the network and included guests.

In the first part of our work, the two different tetrabromo-SBFs (substituted in the *meta* and *para* positions, respectively, relative to the spiro center) were synthesized either by a literature procedure or through a new route. Crystals were grown and the structures were solved. Both structures are close packed, and the molecules are linked together by Br $\cdots$ Ar interactions and also by Br $\cdots$ Br contacts. In the second part of our work, we co-crystallized un-

substituted SBF with small brominated guests that orient 1, 2, 3 or 4 atoms of bromine in distinct directions. The structures of four co-crystals were solved, and analysis reveals the following points: 1) There are at most only a few direct interactions (CH $\cdots$ π) between the SBF units themselves; 2) by engaging in Br $\cdots$ aryl interactions, the brominated guests play a role of connector between SBF units; iii) in this way, Br $\cdots$ aryl interactions direct the packing of the crystal structures.

Keywords: molecular tectonics; Br $\cdots$ Ar interactions; Br $\cdots$ Br interactions; spirobifluorene.

1. Introduction

Molecular tectonics is an efficiently predictive way to obtain organized supramolecular networks in the crystalline state [1]. This strategy uses building blocks called tectons, which are connected together through non-covalent bonds [2]. In general, strong, directional and reliable interactions, as coordination bonds [3] or H-bonds [4] are involved to link the tectons together. An important challenge remains to bring under control the arrangement of tectons in the solid state by using weaker interactions such as $\pi\cdots\pi$, halogen $\cdots$ halogen, halogen $\cdots$ aryl, charge-transfer and CH $\cdots$ π interactions, which are useful in different field of crystal engineering [5]. Recently, the complex task of using C-H $\cdots$ N, C-H $\cdots$ O or -C $\equiv$ C-H $\cdots$ C $\equiv$ C interactions to direct crystallization and to obtain predictable structures has been demonstrated, [6,7] pointing out the necessity to undertake new studies. In this paper, we propose to estimate the ability of Br $\cdots$ aryl interactions to control the self-assembly of tectons derived from 9,9'-spirobi-

fluorene (SBF) derivatives in the crystalline state. Moreover, we want to evaluate the aptitude of Br $\cdots$ aryl interactions to form predictable organized supramolecular networks in the crystalline state through the molecular tectonics strategy. Br $\cdots$ aryl interactions, which are van der Waals type interactions, set up thanks to the ability of the relatively electropositive bromine atom [8] to polarize aromatic ring. Two major components contribute to the stabilisation of a bromine atom near an aromatic ring: the dispersive interaction with the polarizable π -moiety and the coulomb attraction between the bromine and the positively charged hydrogen attached to the arene ring (see Scheme 1). When the angle α is under 60°, van der Waals component of the interaction dominate, whereas α is above this value, Br $\cdots$ aryl contact is more or less a weak hydrogen bond [9]. Desiraju has shown in a significant previous work

that Br $\cdots$ aryl interactions generate interesting supramolecular motifs [10]. In his study, the similarity of the diamond-based crystal structure of tetrakis-(4-bromophenyl)methane **1** and the 1:1 molecular complex of tetraphenylmethane **2** and CBr₄ has been demonstrated. This near identity came up on the one hand because of the interchangeability of the CBr₄ molecular synthon by the Br₄ supramolecular synthon and on the other hand of the ability of the CBr₄ molecule to participate in Br $\cdots$ phenyl interactions (**Scheme 1, a and b**). Br $\cdots$ aryl interactions have also been the topic of interest in numerous studies based on statistical analysis of structural data from the Cambridge Structural Database (CSD) [11]. All these studies contributed to highlight the nature of Br $\cdots$ aryl contacts and also pointed out their important role in the crystal packing. Nevertheless, Br $\cdots$ aryl interactions have not been right away used for molecular

Scheme 1. a and b: representation of the Br₄ supramolecular synthon, c: Br $\cdots$ Ar interaction d: Br $\cdots$ Br interactions.

Scheme 2. Chemical structures of the spirobifluorene tectons

tectonics strategy in the past. In our study, two different approaches have been envisaged. The crystallization of tetrabromo-SBF **3** in a first part, and the co-crystallization of SBF **4** with small brominated molecules **a-d** in a second part (**Scheme 2**). The 9,9'-spirobifluorene derivative's tectons are suitable candidate for this study. First, SBF displays a D_{2d} point of symmetry, is rigid and orient in distinct direction aromatic rings and their substituents. Moreover, SBF derivatives are *a priori* easy to crystallize and are known for making inclusion complexes [12], allowing the formation of desired co-crystals. Finally, these tectons are structurally close to tetraphenylmethane systems, enabling the comparison with Desiraju's previous work.

2. Materials and Methods

2,2',7,7'-tetraamino-3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene](5). To a mixture of 2,2',7,7'-tetraamino-9,9'-spirobi[9H-fluorene] (**6**; 948 mg, 2.518 mmol) and FeCl_3 (0.2848 g, 1.756 mmol) in 150 mL of dry THF at 0 °C, bromine (0.55 mL, 11 mmol) was added. The reaction mixture was stirred for 4.5 hours at 0 °C and was then poured into a mixture of $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL), THF (300 mL) and water (200 mL). After a complete dissolution, the solution was stirred and extracted three times by THF. The organic layers were then washed with NaOH 1M then with brine. The organic layers were combined, dried with Na_2SO_4 , filtered and the solvent was removed under vacuum. The crude product was chromatographed on silica (toluene: CH_2Cl_2 95:5), giving the pure compound **5** (1.5904 g, 91 %) as a white solid: mp > 300 °C; ^1H NMR (DMSO, 400MHz): δ 7.82 (s, 4H), δ 6.10 (s, 4H), δ 5.14 (s, 8H); ^{13}C NMR (DMSO, 75.4 MHz): δ 149.8, 145.2, 131.7, 123.63, 111.2, 108.0, 64.56; FTIR (KBr): ν = 3368, 3316, 3189, 2955, 2923, 2866, 1662, 1615, 1571, 1465, 1420, 1306, 1248, 1025, 1002, 875, 642 cm^{-1} ; MS (FAB) calculate for $\text{C}_{25}\text{H}_{16}\text{N}_4\text{Br}_4$ m/e =691.8, found 692.0.

3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (3). At 65°C, under inert atmosphere, a solution of **5** (151 mg, 0.218 mmol) in DMF (10 mL) was added to a solution

of isoamylnitrite (20 mL, mmol) in DMF (20 mL). The reaction mixture was stirred during 48 hours at 65 °C, then AcOEt (150 mL) was added. Organic layer was washed four times with aqueous HCl 1N then with brine. The organics were combined, dried with Na_2SO_4 , filtered and the solvent was removed under reduced pressure. Resulting oil was dried under vacuum, giving compound **3** as crystals suitable for X-ray analysis (61 mg, 44 %): mp > 286°C; ^1H NMR (DMSO, 400MHz): δ 8.39 (d, 4H, 4J = 2.4), δ 7.33 (dd, 4H, 4J = 2.4, 3J = 10.8), δ 6.62 (d, 8H, 3J = 10.9); ^{13}C NMR (DMSO, 75.4 MHz): δ 145.7, 142.1, 131.1, 125.1, 124.2, 121.5, 63.73; FTIR (KBR): ν = 2961, 2922, 2851, 1636, 1590, 1566, 1523, 1469, 1415, 1384, 1346, 1261, 1093, 1059, 1025, 948, 865, 807, 633 cm^{-1} ; MS (FAB) calculate for $\text{C}_{25}\text{H}_{12}\text{N}_4\text{Br}_4$ m/e =631.8, found 631.9.

X-ray Crystallographic Studies. X-ray diffraction data were collected with Cu KR radiation using a Bruker SMART 2000 CCD or a Bruker Smart 6000 CCD diffractometer equipped with an FR591 rotating anode generator. The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.24 All non-hydrogen atoms were refined anisotropically, except for disordered molecules of included solvent. Hydrogen atoms were placed in ideal positions and refined as riding atoms.

3. Results

3.1 Synthesis and Crystallization. The unsubstituted SBF **4** was synthesized according a literature procedure from the 2-aminobiphenyl [13]. *Para*-substituted tetrabrominated SBF **3** was synthesized through a new synthetic route describe in the **Scheme 3**. From the tetra-amino SBF **6** synthesized *via* a previously described route [14], a bromination step (91 %) followed by a desamination step (44 %) gave the *para*-substituted tetrabrominated SBF **3** in a 40 % overall yield from **6**. Tecton **3** was crystallized from traces of DMF. The co-crystals **4_{b-d}** were obtained by slow evaporation of **4** in the corresponding brominated guest (**b-d**) solution. In the case of **4_a**, as CBr_4 is a solid at

Scheme 3. Synthesis of the tecton **3**.

room temperature (mp = 88-90 °C), hot hexane was used as co-solvent. Slow cooling followed by an evaporation of the solution induced crystallisation of **4_a**.

3.2 Structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (3). Compound **3** crystallized as a close-packed-structure in the *Aba2* space group. Surprisingly, the structure displays no Br...aryl interaction but only Br...Br contacts and weak Br...H bonds [15]. Each molecule is linked to four neighbors through one Br...Br contact (distance of 3.7984(6) Å, see **Figure 1**). The Br...Br interactions were described in the literature by Desiraju through two types, **I** and **II**, depending of the angles (θ_1, θ_2) made between C-Br bonds (see **Scheme 1, d**) [16]. Recently, Desiraju proposed that type **I** are of van der Waals type whereas type **II** arises from a polarization of bromine atoms [17]. Type **II** Br...Br contacts were observed in our case ($\theta_1 = 154.81(8)^\circ$; $\theta_2 = 68.4(9)^\circ$). The distance (3.7984(6) Å) is slightly above the high limit value reported by Navon et al. (3.7 Å max) [18] suggesting that the Br...Br contacts form a fragile intermolecular link in this case. Nevertheless, it is interesting to note that reducing each tectons to spheres lying at their center and joining the net together drive to a parallel superimposition of 2D lattices (see Supporting Information). Each tecton is linked with six molecules through weak Br...H bonds with typical distance values ranging from 3.21 Å to 3.51 Å, acting 6 times as a donor and 6 times as an acceptor (see Supporting Information). Each neighbor forms two interactions of this type with the central moiety. These numerous interactions define a 2D-lattices that are interconnected via longer Br...H links (3.61 Å) and via the Br...Br contacts (see Supporting Information). In the crystal structure of **3**, the packing is driven by the shape of the tecton **3** and thus follow the Kitaigorodskii model [19]. Attested by the long distance between the interacting bromine atoms (i.e. 3.7984(6) Å) the Br...Br contacts probably arise as a consequence of packing of molecules and maybe contribute only a little to the crystal energy. On the contrary, the Br...H bonds display typical distances reported in the literature, creating a consistent link between the tectons. Moreover they are numerous and form a highly connected network, suggesting that they act as an important component in the network's total energy. These results are different of previous observations made by Desiraju in the close tetraphenylmethane system (tecton **1**). In his study, the tecton **1** crystallized in a diamondoid network where the formation of Br₄ supramolecular synthon is the driving force of the packing. The relative flexibility of the tetraphenylmethane core allows the formation of Br₄ clusters in a close packed system. On the other hand, the

formation of such clusters would have probably led to an open system with the more constrain SBF core, and such open systems are disfavored. However, it is important to note that, Br...aryl interactions were not observed in Desiraju's study too. Despite the presence of aromatic rings and bromine atoms, none Br...aryl interactions are observed in the crystal structure. In order to get supramolecular networks based Br...aryl interactions, a second approach, involving unsubstituted SBF **4** as tecton and small brominated molecules, was undertaken.

Figure 1. View of the structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (**3**) showing a central tecton (red) surrounded by its four neighbors (blue). The bromine atoms involved in Br...Br contacts are joined together by broken lines.

3.3 Structure Structures of co-crystals between unsubstituted 9,9'-spirobifluorene and small brominated molecules (4_{a-d}). In the second part of our study, our aim was to find favorable conditions for the establishment of Br...aryl interactions. We decided thus, to prepare co-crystals between unsubstituted SBF **4** and small brominated molecules (**a-d**). This second strategy was undertaken for few reasons: i) the aromatic rings of unsubstituted SBF **4** are more accessible than the corresponding tetra-bromo ii) as the brominated guest molecules are much more smaller than the tecton **4**, the brominated moiety should be less constrain by the crystal packing effects. iii) Desiraju has shown that in the co-crystal made from the unsubstituted tetraphenylmethane **2** and CBr₄ (guest **a**), Br...aryl interactions are directing the packing of the crystal structure and iv) finally, we wanted to see if a correlation between the number of bromine atoms on the co-guest and the network could be deduced. Regarding the literature, the first crystal structure of SBF **4** was reported by Schenk in 1972 [20]. Recently another polymorph and also two

inclusion compounds of SBF **4** with hydroaromatics were reported [21]. In those structures, it is interesting to note that C-H $\cdots\pi$ interactions between adjacent SBFs are the driving force of the packing.

3.4.1 Structure of 9,9'-spirobi[9H-fluorene] co-crystallized with CBr₄ (4_a). In the conditions cited above, the co-crystal **4_a** was obtained. The SBF **4** co-crystallized with four equivalents of CBr₄ (composition 4.4CBr₄) in the tetragonal *P*4₂/*n* space group. Surprisingly, the structure displays no interaction between the SBFs themselves. Indeed, 68 % of the total volume of the crystal is occupied by the CBr₄ molecules and each SBF is surrounded by a total of sixteen CBr₄. Consequently the SBF molecules are insulated. One set of eight neighbors is linked by a combination of Br $\cdots$ aryl and Br $\cdots$ H interactions (CBr₄ in blue, **Figure 2**), the other set being linking exclusively through Br $\cdots$ H bonds (CBr₄ in green, **Figure 2**). In the blue set, two different CBr₄ are connected to the central SBF (Br $\cdots$ Ar_{centroid} distances: 3.4893(13) Å; 3.7319(12) Å and α angles: 21.6(1)°; 5.6(1)° respectively). The short distances and the α values clearly under 60° emphasize the van der Waals attraction character of the Br $\cdots$ aryl interactions between **4** and **a** [22]. The weak Br $\cdots$ H bonds reinforce the link between central SBF **4** and the green set of CBr₄ (distances less than or equal to 3.60 Å, **Figure 2**), this bi-component stabilisation being illustrated by the short centroid's distances between SBFs and CBr₄ (CBr_{4centroid} $\cdots$ SBF_{centroid} equal to 6.50 Å and 5.84 Å).

The second CBr₄ set (CBr₄ in green, **Figure 2**), display only Br $\cdots$ H bonds with the central SBF **4**. The distances are not exceptional with a range of distances going from 3.17 Å to 3.58 Å. However, at least two

Br $\cdots$ H contacts connect each CBr₄ and the central SBF, creating a multiple link. Compared to the first set of CBr₄, the weakness of that mono-component link is illustrated by a centroid to centroid distance almost 2 Å longer for the two different CBr₄ (CBr_{4centroid} $\cdots$ SBF_{centroid} equal to 8.34 Å and 8.26 Å). In the crystal structure **4_a**, each SBF tectons is insulated and each CBr₄ molecule is implied in both type of interaction with at least two SBFs. All these observations clearly demonstrate that the CBr₄ molecules act as connectors between the SBFs **4**. In addition, Br $\cdots$ H contacts and mainly Br $\cdots$ aryl interactions are the complementary stabilization interactions which drive the packing of the crystal structure. Finally, Br $\cdots$ Br contacts are formed between the connectors themselves. With distances more than or equal to 3.82 Å these contacts are weak and once more must probably be the result of crystal packing effects than real interaction.

In the study report by Desiraju, co-crystallization of CBr₄ and the tetraphenylmethane **2** led to a 1:1 molecular complex of formula **2**.CBr₄ (noted **2_a**), which is different to the 1:4 stoichiometry of **4_a**. Moreover, similarly to **3**, a diamondoid network was observed for **2_a**, allowing Desiraju to conclude to an equivalence of the supramolecular synthons **a** and **b** (see **Scheme 1**). In our case, neither the crystal structure of **3** nor **4_a** display a diamondoid network, consequently the equivalence is not observed. However, in **2_a** and **4_a** crystal structures, a similarity is observed: Br $\cdots$ aryl interactions are the driving forces of the packing.

3.4.2 Structure of 9,9'-spirobi[9H-fluorene] co-crystallized with CHBr₃ (4_b). Co-crystal **4_b** was obtained under conditions cited before, and crystallized in the *P*2₁/*n* space group. Two SBF's and four CHBr₃ are

Figure 2. View of the structure of 9,9'-spirobi[9H-fluorene] (**4_a**) showing a central molecule (red) surrounded by two sets of CBr₄ neighbors. The blue set interacts through both Br $\cdots$ aryl (red broken lines) and Br $\cdots$ H interactions (black broken lines) with the central molecule, whereas the green set is only involved in Br $\cdots$ H contacts. Left) View of the interaction of one side. Right). View of the interaction involving the whole central molecule.

present in the unit-cell. In **4_b**, SBF's are connected together through CH $\cdots\pi$ edge to face aromatic interactions with distances ranging from 2.63(5) Å to 2.77(3) Å. Each tecton forms CH $\cdots\pi$ interactions with three neighbors resulting in a superimposition of 2D honeycomb networks (**Figure 3**). Each SBF also interacts with twelve CHBr₃ molecules. Considering the interactions between one central SBF and the twelve neighbors, CHBr₃ molecules can be classified in three categories: i) Seven form exclusively weak Br $\cdots$ H bonds with the central SBF (Br $\cdots$ H distances less or equal to 3.87(3) Å, molecules in green in **Fig. 4**); ii) four CHBr₃ molecules are involved in both Br $\cdots$ aryl (Br $\cdots$ Ar_{centroid} distances going from 3.37(7) Å to 3.83(7) Å and α between 1.0(2)° and 22.4(9)°) and Br $\cdots$ H contacts (molecules in blue in Fig 4) and iii) one CHBr₃ forms a CH $\cdots\pi$ interaction with the central tecton ($d =$

2.64(9) Å and 2.43(0) Å, molecules in purple, **Fig. 4**). If the average of center to center distance for category i) is noted $d(i)$, it is important to note that $d(i) > d(ii) > d(iii)$ (i.e. 8.35(4) Å > 6.42(7) Å > 5.02(0) Å). The decreasing of the center to center distances between central tecton and the CHBr₃ is consistent with an increasing of the strength of the link. Each CHBr₃ molecule interacts at least with two SBF's by combining two types of interaction among the three cited upon. On the one hand, the connection of SBFs through CHBr₃ reinforce the 2D lattices, and on the other hand the CHBr₃ molecules create links between the 2D sheets, as a result driving to a highly connected 3D network (see Supporting Information). In consequence, in the crystal structure of **4_b**, CHBr₃ molecules act as connectors which link the SBF's together.

Figure 3. Left: View of the structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (**4_b**) showing a central tecton (red) surrounded by its three neighbors (blue). Right: View of the superimposition of the 2D honeycomb networks made by the connected SBF units.

Figure 4. View of the structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (**4_b**) showing the two different central tectons (red) surrounded by three sets of CHBr₃. The green set forms exclusively weak Br $\cdots$ H bonds with the central SBF units, the blue set is involved in both Br $\cdots$ aryl and Br $\cdots$ H contacts while the purple one forms also CH $\cdots\pi$ interaction with the central tecton.

3.4.3 Structure of 9,9'-spirobi[9H-fluorene] co-crystallized with CH₂Br₂ (4c). The tecton **4**, dissolved in **c** was found to crystallize in the $P2_1/n$ space group. The crystal displays the well defined composition $4 \cdot \text{CH}_2\text{Br}_2$. One SBF and one CH₂Br₂ molecules are present in the unit-cell. As in the **4_b** crystal structure, tecton **4** form CH $\cdots\pi$ (arene) interactions, two as donor and two as acceptor, with SBF's neighbors with distances less or equal to 2.82(8) Å. But in that case, each SBF is connected to four neighbors with center to center intermolecular distances of 7.61(7) Å and 7.66(7) Å, as a consequence driving to a superimposition of quasi planar 2D square grid lattices (Fig. 5, right). On the other hand each SBF is also connected to five

Figure 5. top: View of the structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (**4_c**) showing a central tecton (red) surrounded by its four neighbors (blue). The CH $\cdots\pi$ interactions appear as broken lines. Bottom: the quasi planar 2D square grid lattices formed by the SBF units in the crystal structure of **4_c**.

CH₂Br₂ molecules. In the plan of 2D lattice, SBF is connected through CH $\cdots\pi$ interaction to one CH₂Br₂ ($d = 2.80(3)$ Å) and through Br $\cdots$ aryl interactions with another two CH₂Br₂ ($d = 3.58(5)$ Å; $\alpha = 9.2(6)^\circ$ and $3.90(9)$ Å; $\alpha = 9.1(5)^\circ$, Fig. 6), whereas out of the plan the central SBF forms weak Br $\cdots$ H bonds with the two last CH₂Br₂ molecules ($d = 3.70(5)$ Å or less, Fig. 6). Even though there are intermolecular interactions (i.e.

Figure 6. View of the structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (**4_c**) showing a central tecton (red) surrounded by its six brominated neighbors.

CH $\cdots\pi$), the brominated molecules play a role of connectors in the network. Indeed, on one hand the three CH₂Br₂ in the plan of 2D lattice reinforce the link between the tectons through CH $\cdots\pi$ and Br $\cdots$ aryl, on the other hand the two other CH₂Br₂ molecules connect the 2D lattice together through weak Br $\cdots$ H bond, creating a highly branched 3D network (see Supporting Information). Compared to **4_a**, replacing one (**4_b**) or two (**4_c**) bromine atom(s) by hydrogen atom(s) on the co-guest had many consequences. First, less Br $\cdots$ aryl interactions per SBF molecule have been observed (eight (**4_a**) vs. four (**4_b**) vs. two (**4_c**)). Then, the CH moiety of the brominated guest allows the establishment of CH $\cdots\pi$ interaction with SBF, nevertheless not replacing all the missing Br $\cdots$ aryl. As a consequence, the volume occupied by brominated guests is less important in the crystal (68 % (**4_a**) vs. 45 % (**4_b**) vs. 26 % (**4_c**)), making the SBF tectons closer, and as a result this generates interactions between tectons themselves.

3.4.4 Structure of 9,9'-spirobi[9H-fluorene] co-crystallized with EtBr (4d). In order to complete our study, a crystallization with a mono-brominated guest was undertaken. As CH₃Br was too volatile ($E_b = 4^\circ\text{C} / 760 \text{ mm Hg}$), EtBr **d** was used instead. By slow evaporation of a solution of **4** in **d**, single crystals were obtained. The analysis through X-Ray diffraction revealed an inclusion compound of the well defined formula **4.d** crystallized in the $P2_1/n$ space group. The unit-cell parameters show that **4_d** is isostructural to **4_c**. In addition to the space group, the unit-cell parameters and the stoichiometry both structures display other common

structural features. Indeed, through two different CH $\cdots\pi$ interactions each SBF is connected to four SBFs, two as donor and two as acceptor ($d = 2.74(7)$ Å and $2.64(6)$ Å) driving to a near superimposition of 2D lattices (see Supporting Information). Moreover, five brominated guests, three in the plan of 2D sheet and two out, interact with the central tecton by forming two CH $\cdots\pi$ $d = 2.93(5)$ Å and $d = 2.97(3)$ Å one Br $\cdots$ aryl interaction ($d = 3.69(2)$ Å; $\alpha = 7.1(4)^\circ$ and weak Br $\cdots$ H bonds ($d = 3.62(3)$ Å or less, see Supporting Information). Nevertheless, in the case of **4_d**, it is important to note that a CH $\cdots\pi$ is substituted to a Br $\cdots$ aryl interaction to connect the tecton and the guest (see Fig. 7), suggesting a supramolecular equivalence between a methyl group and a bromine atom. This equivalence was already put in evidence in the past with a chlorine atom [23]. In addition, each EtBr is connected to six SBFs and consequently plays, as CH₂Br₂, a role of connector between tectons. The resulting network of **4_d** forms nearly the same superimposition of 2D square grid lattices than **4_c** connected together through weak Br $\cdots$ H bonds (intertectonic distances are slightly different, $d = 7.616$ Å vs $7.61(7)$ Å and $7.66(7)$ Å).

Figure 7. View of the structure of 3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (**4_d**) showing a central tecton (green) surrounded by its six brominated neighbors.

3.5 Structure of 2,2',7,7'-tetraamino-3,3',6,6'-tetrabromo-9,9'-spirobi[9H-fluorene] (5**).** During the synthetic process, single crystals of **5** were obtained in CH₂Cl₂ and the X-Ray structure was solved [24]. In the structure of **5**, the H-bonds involving the NH₂ groups strongly link the SBFs together and build a 2D network. The packing of **5** is oriented through these “strong”

H-bonds, the other interactions (i.e. weak H-bonds and Br $\cdots$ Br contacts) resulting probably more of the crystal packing effects. Moreover, it is important to note that the halogenated guests fill the empty spaces and don't act as a connector in that case. As expected, in the crystal structure of **5**, in presence of groups able to form “strong” H-bonds (the amino groups), interactions creating by bromine atoms play only a second role in the packing of the structure.

4. Conclusion

In order to evaluate how Br $\cdots$ aryl interactions can be used in molecular tectonics strategy and particularly for the design of supramolecular networks in the crystalline state, two strategies involving SBF derivatives tectons were undertaken. The first one, engaging the tetrabrominated SBF **3**, has revealed some interesting points. Orienting bromine atoms and aromatic rings in distinct directions of space in order to control a supramolecular assembly through Br $\cdots$ aryl interactions in the crystalline state is not a self-important condition. Indeed, in the case of **3**, Br $\cdots$ aryl interactions seems to be not strong enough to constrain the assembly toward an energetically expensive open network, and the system was instead driven to a more favored close compact structure. In the second part of our study, co-crystals between unsubstituted SBF **4** and brominated guests were analyzed. First, it is important to note that four crystals with Br $\cdots$ aryl interactions among the main stabilizing interactions were obtained through the co-crystallization way. The success of this strategy is probably due on the one hand, to the less constrain small brominated moiety, and on the other hand to the better accessibility of SBF's aromatic rings, driving to a good complementarity between the co-guests and the tectons. Moreover, the networks present features that follow a certain logic regarding the number of bromine atoms on the co-guest. Decreasing the number of bromine atoms (CBr₄, CHBr₃ and CH₂Br₂) cut down the number of Br $\cdots$ aryl interactions *per* tectons (respectively 8, 4 and 2). In addition, the number of brominated guests *per* tecton decreases (respectively 4.4CBr₄, 4.2CHBr₃ and 4.CH₂Br₂) and consequently, less volume is occupied by the brominated guest (respectively 68 %, 45 % and 26 %). In the three structures **4_{a-c}**, the brominated guests play a role of connector between the SBFs tectons. On the one hand, in the **4_b** and **4_c** structures, they reinforce the 2D sheets formed by CH $\cdots\pi$ interactions between SBFs and connect these 2D lattices together and on the other hand, in the case of CBr₄ (**4_a**), no direct interactions were observed between SBFs. Through Br $\cdots$ aryl interactions, CBr₄ ensures the cohesion of the supramolecular edifice by connecting the tectons

together. Similarly to the structure of **2_a** obtained by Desiraju, Br $\cdots$ aryl interactions orient the packing of **4_a**. Nevertheless, as our structures **3** and **4_a** are not diamondoid systems, the equivalence of supramolecular synthons **a** and **b** (see Scheme 1) was not observed. The case of the mono-brominated guest EtBr is different. As previously described in the literature for a chlorine atom, the isostructural crystals **4_c** and **4_d** allow us to put in evidence the supramolecular equivalence between a bromine atom and a methyl group, and as a consequence making EtBr a non-suitable model of CH₃Br. As a general conclusion, this study emphasizes the importance of Br $\cdots$ aryl interactions, the Br $\cdots$ Br and the Br $\cdots$ H playing only a second role in the tectons arrangement. Indeed, new organized and to a certain extent predictable supramolecular networks using Br $\cdots$ aryl interactions as the driving force of the packing have been obtained. In the absence of strong H-bond promoting groups, and on the other hand in non Kitaigorodskii case, Br $\cdots$ aryl interactions can be a useful tool for the design of supramolecular networks by using the strategy of molecular tectonics. As an application of this concept, development of new molecular hosts derived from SBF and based on Br $\cdots$ aryl interactions are presently attempted in our group.

Acknowledgement

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Ministère de l'Éducation du Québec, the Canada Foundation for Innovation, and the Canada Research Chairs Program for financial support.

Supporting Information Available: Further structural details, including ORTEP drawings and tables of crystallographic data, Structure of **5**, and bibliographic references. This material is available free of charge via the Internet at http://ccaasmag.org/chem_2011/vol1/Darbost_halogenAryl_supporting-info.pdf

References

- [1] For a review, see: Wuest, James D. *Chem. Commun.* **2005**, 5830. <http://dx.doi.org/10.1039/b512641j>
- [2] Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696. <http://dx.doi.org/10.1021/ja00012a057>
- [3] For recent reviews, see: a) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. <http://dx.doi.org/10.1039/b200393g>; b) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi,

- M.; Kim, J. *Nature* **2003**, *423*, 705. <http://dx.doi.org/10.1038/nature01650>
- [4] For a review of hydrogen bonding in the solid state, see: Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48. [http://dx.doi.org/10.1002/1521-3773\(20020104\)41:1<48::AID-ANIE48>3.0.CO;2-U](http://dx.doi.org/10.1002/1521-3773(20020104)41:1<48::AID-ANIE48>3.0.CO;2-U)
- [5] For reviews of weak interactions, see: a) Gautam R. Desiraju, *Chem. Commun.* **2005**, 2995. <http://dx.doi.org/10.1039/b504372g>; b) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565. <http://dx.doi.org/10.1021/ar010054t>; c) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999. For a review of aromatic interactions, see: d) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651. <http://dx.doi.org/10.1039/b008495f>; For a recent example of charge-transfer interaction in crystal engineering, see: Lindeman, S.V.; Hecht, J. and Kochi, J.K. *J. Am. Chem. Soc.* **2003**, *125*, 11597. <http://dx.doi.org/10.1021/ja030299w>
- [6] Demers, E.; Maris, T.; Cabana, J.; Fournier, J. -H.; Wuest, James D. *Cryst. Growth Des.* **2005**, *5*, 1237. Maly, K. E.; Maris, T.; Gagnon, E.; Wuest, J. D. *Cryst. Growth Des.* **2006**, *6*, 461.
- [7] Laliberté, D.; Maris, T.; E. Ryan, P.; Wuest, J. D. *Cryst. Growth Des.* **2006**; ASAP Article.
- [8] Lieberman, H. F.; Davey, R. J.; Newsham, D. M. T. *Chem. Mater.* **2000**, *12*, 490. Adams, H.; Cockroft, S. L.; Guardigli, C.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Spey, S. E.; Urch, C. J.; Ford, R. *Chem. Bio. Chem.* **2004**, *5*, 657.
- [9] Swierczynski, D.; Luboradzki, R.; Dolgonos, G.; Lipowski, J.; Schneider, H.-J. *Eur. J. Org. Chem.* **2005**, 1172. <http://dx.doi.org/10.1002/ejoc.200400446>
- [10] Reddy, D. S.; Craig, D. C.; Desiraju, G. R. *J. Am. Chem. Soc.* **1996**, *118*, 4090. <http://dx.doi.org/10.1021/ja953373m>
- [11] For recent studies see: Swierczynski, D.; Luboradzki, R.; Dolgonos, G.; Lipowski, J.; Schneider, H.-J. *Eur. J. Org. Chem.* **2005**, 1172. Prasanna, M.D.; Guru Row, T.N. *Crystal Engineering* **2000**, *3*, 135.
- [12] Fournier, J.-H.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2004**, *69*, 1762. <http://dx.doi.org/10.1021/jo0348118>
- [13] Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906. <http://dx.doi.org/10.1021/jo960897b>
- [14] Fournier, J.-H.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2004**, *69*, 1762.

- <http://dx.doi.org/10.1021/jo0348118>
- [15] Desiraju, G. R., Steiner, T. *The Weak Hydrogen Bond*, Oxford university Press, Oxford, **1999**.
- [16] Pedireddi, V. R.; Shekhar Reddy, D.; Satish Goud, B.; Craig, D. C.; David Rae, A.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2*, **1994**, 2353. <http://dx.doi.org/10.1039/p29940002353>
- [17] Mall Reddy, C.; Kirchner, M. T.; Gundakaram, R. C.; Anantha Padmanabhan, K.; Desiraju, G. R. *Chem. Eur. J.* **2006**, *12*, 2222. <http://dx.doi.org/10.1002/chem.200500983>
- [18] Navon, O.; Bernstein, J.; Khodorkovski, V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 601. <http://dx.doi.org/10.1002/anie.199706011>
- [19] Kitaigorodskii, A. I., *Molecular Crystals and Molecules*, Academic Press, New York, **1973**.
- [20] Schenk, H. *Acta Cryst.*, **1972**, *B28*, 625.
- [21] Douthwaite, R. E.; Taylor, A.; Whitwood A. C. *Acta Cryst.*, **2005**, *C61*, 328.
- [22] Swierczynski, D.; Luboradzki, R.; Dolgonos, G.; Lipowski, J.; Schneider, H.-J. *Eur. J. Org. Chem.* **2005**, 1172. <http://dx.doi.org/10.1002/ejoc.200400446>
- [23] Nakai, Y.; Yamamoto, G.; Ooki, M. *Chem. Lett.* **1987**, 89. <http://dx.doi.org/10.1246/cl.1987.89>
- [24] a detailed description of the crystal structure of **5** is reported in the Supporting Information.