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Two-Dimensional Bricklayer Arrangements of Tolans Using Halogen Bonding Interactions

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Diphenylacetylene (tolan) derivatives with self-complementary aryl halides and halogen bond-accepting nitriles form 2D bricklayer packing motifs when halogen bonding occurs. When halogen bonding is absent, as occurred with fluorinated aryl bromides, the molecules adopt other packing motifs. These results suggest halogen bonding is potentially useful for producing rarely observed 2D bricklayer motifs in organic semiconductors.

The intermolecular arrangements of molecules with highly delocalized, π-conjugated structures are critical to their solid-state properties and performance as semiconductors. Intermolecular electronic coupling between molecules in the solid state is key, for example, to charge-carrier mobility in field-effect transistors as thin films or single crystals.[1,2] Edge-face interactions, such as C-H/π interactions, often lead to herringbone-type arrangements, which in many cases precludes effective electronic coupling between the π-systems of individual molecules. Overcoming the tendency for candidate organic semiconductors to adopt herringbone packing motifs is therefore an important goal for organic electronics.[3] There are few generally applicable strategies, however, for the rational design of molecules to accomplish this goal.

Trialkylsilylethynyl-substituted pentacenes, heterocyclic analogs thereof, and structurally related compounds show predictable trends of herringbone, 1-D slipped-stack, and 2-D bricklayer packing that correlate with the size of the trialkylsilyl groups.[4-8] A number of studies have demonstrated that organic semiconductors with 2-D bricklayer packing generally yield superior charge carrier mobilities to those with herringbone or 1-D slipped-stack packing.[9-13] An alternative approach to overcoming edge-face interactions would be to design molecules with edge-edge interactions that could compete with edge-face interactions. Hydrogen bonding is one class of edge-edge interactions of which there are several examples that yield intermolecular overlap of π-orbitals of highly conjugated small molecules.[14-18]

In comparison to hydrogen bonding, halogen bonding (XB) is a less often encountered, but increasingly popular, non-covalent interaction.[19-22] Halogen bonds are interactions between areas of negative potential, such as nitrogen-based lone pairs of electrons, and areas of positive potential on large halogens, most often Br and I, located directly opposite of the carbon-halogen bond (the σ-hole); the resulting n-σ* interactions are more highly directional than hydrogen bonds.[23,24] XB has been used in a number of functional materials, including cocrystals and gels.[25,26] In the class of highly delocalized organic molecules, reports include self-complementary diarylethylenes,[27-29] diarylacetylenes,[30] phenoxy-boron subphthalocyanines,[31] azobenzenes,[32] and co-crystals of stilbenes and diiodinated aromatics,[33-35] as well as a number of studies on halogen bonding in TTF derivatives.[36] Recently, multi-point halogen bonds were discovered in crystals of dihalodiimides,[37] and weak halogen bonding was discovered in halogenated N-heterocyclic acenes.[38] Herein we describe the dependence of packing motif on chemical structure of simple models for highly delocalized rigid rods—diphenylacetylene derivatives—with self-complementary halogen bonding substituents.

Two observations provided initial inspiration for this work: i) the crystal structures of *p*-halobenzonitriles, which comprise close packed, infinite one dimensional chains of molecules, with N•••X halogen bonds along the axes of the one dimensional chains,[39-41] ii) C-Br and C-I bonds are present in many synthetic intermediates of conjugated materials because of the prevalence of cross-coupling reactions in their preparation. We therefore designed a series of diphenylacetylenes (tolans), with the hypothesis that halogen bonding between the 4 and 4′ positions would yield close-packed,

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one-dimensional chains. Chart 1 shows the chemical structures of diphenylacetylenes **1**-**6**, all of which contain benzonitrile rings. Five of the structures (**1**-**5**) have potential halogen bond donating moieties, from the strongly electropositive tetrafluoroiodide **1** to the weakly electropositive non-fluorinated bromide **5**; control molecule **6** has no halogens. Several studies have established hierarchies of halogen bond donors represented in our molecules as the following: **1** > **3** > **2** > **5**.[42,43] We prepared all compounds with Sonogashira reactions between either i) 4-ethynylbenzonitrile and appropriate aromatic halides (for **1**-**5**) or ii) 4-iodobenzonitrile and phenylacetylene (**6**). A stoichiometric excess of symmetric dihalide prevented a significant quantity of the three-ring phenylene-ethynylene byproduct from forming in the syntheses of **1**-**4**. The non-fluorinated tolans (**2**,[44] **5**,[45] and **6**[46]) are known; compounds **1**, **3**, and **4** have not been reported.

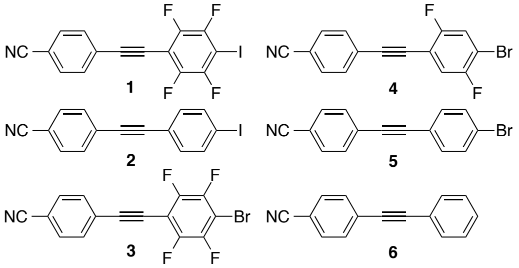

Chart 1. Diphenylacetylene derivatives with self-complementary halogen bonding moieties (**1**-**5**) and a control molecule lacking any halogens (**6**).

We were successful in growing crystals suitable for X-ray crystallography of all compounds listed in Chart 1. Table 1 summarizes some of the key structural parameters obtained from these crystal structures. Figure 1 shows the X-ray crystal structure of non-fluorinated compounds that have self-complementary benzonitrile and iodine (**2**) or bromine (**5**) on opposite ends of the molecules. Molecules **1**, **2**, and **5** arrange in crystal structures similar to analogous *p*-halobenzonitriles:[40] i) there is clear N•••X halogen bonding between the Lewis basic nitrile and the Lewis acidic σ-hole of iodine or bromine as characterized by linear (179-180°) N•••X-C angles and N•••X distances approximately 10–16% less than the sum of their van der Waals radii (Table 1); ii) the halogen bonds between the termini of molecules yield infinite one-dimensional chains of molecules in the direction of their long axes; and iii) the linear chains pack into two-dimensional arrays. The conjugated backbone of **1**, **2** and **5** are somewhat twisted, with 19-22° torsional angles between the two rings in both structures. Unlike *p*-iodobenzonitrile, there is no "roll"—displacement between chains in these arrays along their short axes—in the structures of **2** or **5**. In addition, the lengths of the tolans enables each molecule to participate in cofacial interactions with four other molecules, two from each adjacent one-dimensional chain, with minimal inter-chain C•••C distances of 3.43 Å (**2**) and 3.34 Å (**5**) between rings rotated towards each other. With the exception of compound **2**, which shows several extra peaks in its powder diffractogram, there is good agreement between the X-ray powder diffractograms calculated from the single crystal structures of **1**, **2**, and **5** and those that were measured experimentally (ESI).

Table 1. Relevant Crystallographic and Theoretical Parameters of **1-5**

	XB?	$d_{N\cdots X}$ (Å)	$d_{N\cdots X}/\Sigma r_{vdw}$	V_{max} (I, Br)	V_{max} (ArX face)
1	Yes	2.97	0.84	100.	58.5
2	Yes	3.16	0.90	60.6	-11.1
3	No	-	-	83.5	62.5
4	No	-	-	62.7	30.4
5	Yes	3.07	0.90	43.3	-8.6

All potentials given in kJ/mol

The resultant structures are two-dimensional bricklayer arrangements of molecules, which are uncommon for conjugated molecules, but are reported to be advantageous for charge transport in organic field effect transistors in some circumstances. Additional non-covalent interactions of the halogen atoms exist between 2D brickwall arrays, in these cases between their negatively charged areas (C-X•••H angles = 84°-87°) and the edges of aromatic rings ($d_{I\text{-}H}$ = 3.07 Å in **2**, $d_{Br\text{-}H}$ = 2.92 Å in **5**). Compound **1**, an analog of **2** that has four fluorine atoms on the iodoarene instead of four hydrogen atoms, shows a similar packing motif to **2** and **5**: 1-D chains along the long molecular axis that also contain the halogen bond axis, packed into 2-D bricklayers. In comparison to **2**, a smaller N•••I distance (2.955 Å) along the chains is consistent with a stronger halogen bond of the more electropositive tetrafluoroiodide, while a smaller minimal C-C distance between chains in each bricklayer stack (3.37 Å) reflects strong cofacial interactions between arenes and fluorinated arenes. In addition, the crystal structure of **5** shows evidence of some disorder with respect to the direction of packing of chains (parallel or antiparallel), as inversion twinning occurs in its structure. Although the carbon-nitrogen bond length of the nitrile of **2** is significantly shorter than expected (1.026 Å), we note no other crystallographic evidence for disorder in this structure.[40] Not surprisingly, molecule **6** does not crystallize into a 2D bricklayer packing motif; edge-face interactions dominate its herringbone packing. In addition, the experimentally determined powder X-ray diffractogram of **6** shows excellent agreement with that calculated from the single-crystal structure.

Single crystal structures **3** or **4** do not show N•••Br halogen bonding; each of these molecules have multiple fluorine atoms on the bromoaromatic rings, which we prepared with the hypothesis that the more positive σ-hole on Br would lead to stronger observed halogen bonding than in **5**, as we observed in the comparison of **1** and **2**. In contrast, the bromine atoms in the crystal structure of **3** do not interact with the nitrile group, which instead participates in σ-π* interactions with electropositive carbon atoms on fluorinated rings of nearby molecules; these edge-face interactions preclude the formation of 2D bricklayers. Electrostatically favorable contacts of the bromine atoms of **3** also involve the tetrafluorinated ring, with bromine interacting with i) electronegative fluorine atoms (d = 3.09, 3.14 Å, θ = 143°, 145°)[47] and ii) electropositive carbon atoms (d = 3.46-3.50 Å, θ=82°-105°).

Powder X-ray diffraction analysis of **3** shows clear polymorphism, as the experimental powder diffractogram is different from that calculated from single crystal structure of **3** (ESI).

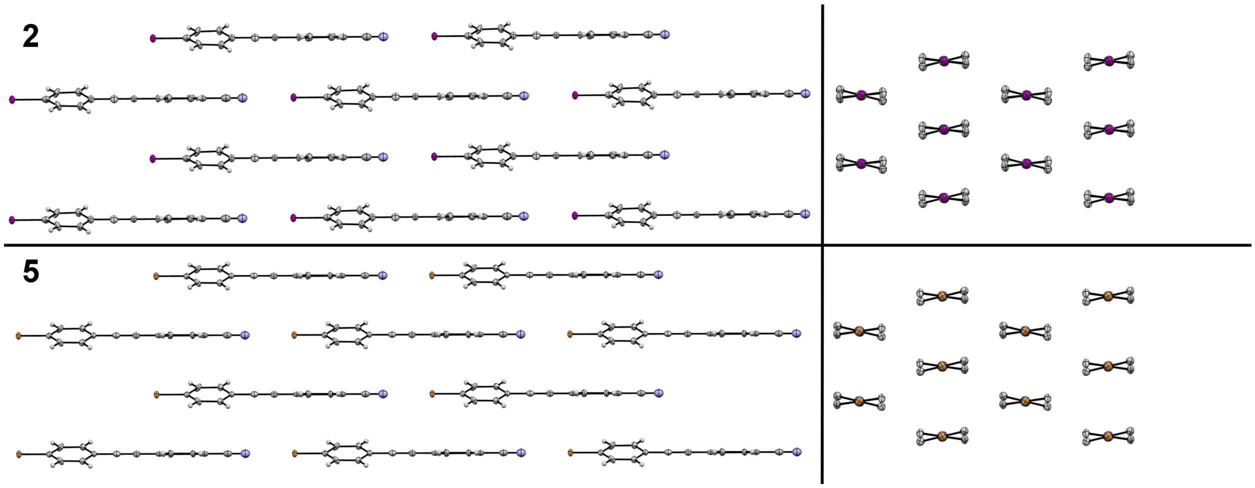

Figure 1. X-ray crystal structures of compounds **2** and **5**, with thermal ellipsoids shown at 50% probability. *Left*: The 2-D brickwork structure of each in the crystallographic *bc* plane; *Right*: Viewed along the crystallographic *c* axis, with hydrogen atoms omitted.

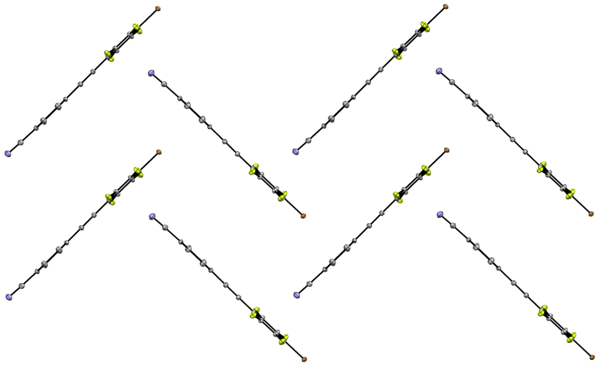

Figure 2. Packing of **3** in a single crystal, viewed along the crystallographic *a* axis, with hydrogen atoms omitted for clarity and with thermal ellipsoids shown at 50% probability. Edge-face interactions between the nitrogen of the nitrile group and the electron-poor face of the fluorinated arene contribute to herringbone-like packing.

We interpret these different diffractograms to be indicative of polymorphism of **3**, highlighting a delicate balance between different non-covalent interactions. Although an effort to reduce the electropositive nature of the face of the tetrafluorinated ring of **3** by preparing difluorinated **4** did result in the absence of significant edge-face interactions and the long axes of all the molecules pointing along the same direction, the bromine atoms of **4** showed no significant short contacts. Instead, each nitrile of **4** participates in hydrogen bonds with two C-H bonds,[48] which together with cofacial interactions between the fluorinated and non-fluorinated rings yielded a 1-D slipped-stack arrangement.

To help us understand structure-property relationships, we calculated the molecular electrostatic potential surfaces of all molecules, using crystallographically-determined geometries, at the DFT level. In all cases, the potentials on the end of the nitrile groups are strongly negative. The trend in maximum positive electrostatic potential at the iodine or bromine (see Table 1) for **1**-**5** matches the trend reported for similarly substituted compounds:[42,43] i) fluorinated arenes having more positive σ-holes on I or Br than those without fluorine atoms, ii) iodides have more positive σ-holes than

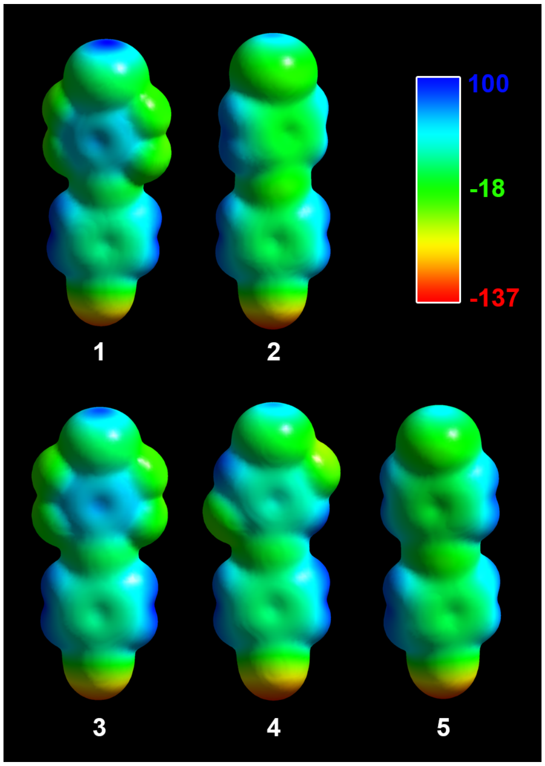

Figure 3. DFT calculated electrostatic potential maps of **1**–**5**, using crystallographically determined geometries and the B3LYP/6-311+G(d,p) basis set. Iodine was treated with the B3LYP/DGDZVP basis set. Scale bar is in kJ/mol.

analogously substituted bromides, and iii) tetrafluorinated aryl bromides have more electropositive σ-holes than non-fluorinated aryl iodides. Although fluorination does indeed increase the positive potential of the σ-holes of **1**, **3**, and **4**, it also increases the positive potential at other locations on the molecular surface, particularly the face of the haloarene, but also on the hydrogen atoms on the edges of both rings. These other areas of positive potential are not sufficiently charged to compete with N•••I halogen bonding, as evidenced by the crystal structure of **1**; they do disrupt, however, the N•••Br halogen bonding present in non-fluorinated bromide **5**, yielding instead edge-face (**3**) and other edge-edge (**4**) interactions of the nitriles in spite of the deeper σ-holes (by 20–30 kJ/mol) on Br of single crystals of these compounds. Therefore, considering the nitrile and σ-holes of these compounds as point charges with magnitude equal to their calculated maximum charge does not sufficiently predict the relative behavior of **3**, **4**, and **5**—i.e., that single crystals of **3** or **4** do not show halogen bonding while **5** does, This observation highlights that more positive σ-holes do not necessarily favor the observation of halogen bonding.

We draw two primary conclusions from this work: i) all benzonitrile-based diphenylacetylene molecules that showed N•••X halogen bonding (**1**, **2**, and **5**) between their long-axis termini showed 2-D brickwork packing motifs, while those molecules that did not show this interaction adopted other packing motifs; ii) while increasing the positive potential of the σ-hole of the aryl iodide through fluorination led to a shorter N•••I halogen bond, fluorination actually disrupted N•••Br halogen bonding by creating other sites of positive potential that interact with the Lewis basic nitrile. More broadly, halogen bonding therefore presents an opportunity to discover other organic semiconductors that adopt 2-D brickwork structures in the solid state. Such packing motifs, although reported in some instances to be highly beneficial to semiconducting properties, are rare in the field of organic semiconductors, as their rational design is currently possible only in narrowly defined cases. This work also highlights how the delicate balance of non-covalent interactions can change resulting arrangement of molecules in a crystal dramatically.

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Notes and References

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