

Influence of Halogen Bonding Interactions in Crystalline Networks of Tetraarylethylene Halobenzoyl Esters

Published as part of the Crystal Growth & Design virtual special issue on Halogen Bonding in Crystal Engineering: Fundamentals and Applications.

Pradeep P. Kapadia, Dale C. Swenson, and F. Christopher Pigge*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States

Supporting Information

ABSTRACT: Solid state halogen bonding interactions have been examined in structurally similar tetratopic haloarenes bearing a common tetraphenylethylene core. This study was designed with the aim of providing insight into the relative importance of fundamental solid state halogen bonding interactions (i.e., halogen…halogen, halogen… π , and halogen…



carbonyl) in systems devoid of strong hydrogen bonding groups. The substrates used in this study all featured four halobenzoate substituents (halogen = Br or I) attached to the four para positions of tetraphenylethylene with conformationally flexible ester linkages. A total of nine crystal structures from five different tetraarylethylene substrates were obtained. While distinct and unique X…O and X… π halogen bonding interactions were identified in each structure, all structures displayed nominally similar packing arrangements generally consisting of one-dimensional ribbons aligned to generate non-interpenetrating two-dimensional sheets. This feature may be a consequence of extensive edge-to-face arene—arene interactions found in each structure and may indicate a greater structure-determining role for aryl-H… π interactions relative to halogen bonding contacts in this system.

INTRODUCTION

Halogen bonding is a noncovalent interaction that takes place between halogen atoms, functioning as electrophilic species, and neutral or anionic electron donors.^{1,2} Organic halides feature an anisotropic distribution of electron density around halogen atoms such that regions of positive electrostatic potential (sometimes referred to as the "sigma hole")³ result along the axes of C-X bonds. Halogen bonding interactions are principally electrostatic in nature and are generally weaker than hydrogen bonds, but they are highly directional in that Lewis bases (B) approach the halogen bond donor (C-X) in a roughly linear fashion (i.e., $C-X \cdots B$ angle \sim 180°). The strength of organic halogen bonding interactions can be altered by neighboring substituents, particularly electron withdrawing groups, as these substituents increase the electrophilicity of halogen bond donors.⁴ Organohalogens also possess regions of negative electrostatic potential along the equator of the C-X bond. Consequently, halogens can display amphiphilic character by acting as both electron acceptors and electron donors in halogen bonding interactions.⁵ Experimental data from solid, liquid, and gas phase studies confirm theoretical predictions that halogen bond donor ability increases in the order of Cl < Br < I, a trend that also correlates with halogen polarizability.² Organofluorines, however, do not typically display halogen bonding properties due to the small size, extreme electronegatvity, and limited polarizability of fluorine atoms. The hybridization of carbons to which halogens are attached also affects halogen bonding ability in the order $C(sp)-X > C(sp^2)-X > C(sp^3)-X$.⁶

The importance of halogen bonding as a means to direct or influence intermolecular recognition and self-assembly processes in organic materials has been demonstrated in a range of research areas. Similar to hydrogen bonding, peripheral halogen groups in a molecule can effectively function as "sticky sites" that direct intermolecular associations of larger supramolecular assemblies. Thus, halogen bonding can play key roles in fields where the design and manipulation of aggregation phenomena are important. Toward this end, halogen bonding interactions have been exploited in mediating solid state assemblies of supramolecular architectures,⁷ liquid crystals,⁸ organic semiconductors,⁹ magnetic materials,¹⁰ nonlinear optical (NLO) materials,¹¹ and templates for solid state synthesis.¹² Halogen bonds have also been observed in solution phase in the context of functional molecular receptors¹³ and in biological systems.¹⁴

Despite their significance, there are many fundamental aspects of halogen bonding interactions that remain to be elucidated. In particular, the relative importance of different types of halogen bonding interactions in polyfunctional organohalogens is not well-defined. As part of studies aimed at determining the relevance of specific halogen bonding synthons as a function of molecular structure, we have previously reported the preparation and structural characterization of conformationally flexible tritopic haloarene derivatives

```
Received:July 29, 2011Revised:December 14, 2011Published:December 21, 2011
```

of general structures 1-3.¹⁵⁻¹⁷ While common halogen bonding motifs in the chloro and bromo derivatives were not evident, extensive bifurcated halogen bonding interactions in the iodo-substituted congeners were observed across all substrates. These interactions took the form of I···I/I···O=C interactions involving amphiphilic iodo substituents in 1 and 2, while iodo groups in 3 were found to function as bifurcated halogen bond donors toward both O=C and arene π functionalities. Generation of this latter synthon assisted in formation of trimeric arrays that further assembled into hexagonal inclusion complexes with solvent-accessible channels of nanoscale dimensions.¹⁷ We have now extended these studies to include structural characterization of tetratopic haloarenes (X = Br, I) affixed to a tetraphenylethylene core (4).

We are interested in utilizing derivatives of tetraphenylethylene (TPE) as starting materials in supramolecular approaches toward a variety of functional materials. Substituted TPE frameworks can be



conveniently prepared by straightforward synthetic transformations so that functional groups important in intermolecular interactions can be easily incorporated.¹⁸ Many derivatives of TPE are known to possess interesting opto-electronic properties (such as low redox potentials, solid state fluorescence, and aggregationinduced emission) that further contribute to the attractiveness of TPEs in supramolecular chemistry.^{19,20} For example, aggregationinduced emission properties of TPEs have been exploited in construction of solution-phase fluorescent sensors for metal ions and biomolecules.^{21,22} Similarly, we have reported pyridinesubstituted TPE derivatives that display switchable emission as a function of solvent and pH.²³ We have also prepared solid state organic semiconducting assemblies mediated by hydrogen bonding between a TPE-based tetracarboxylic acid and various bis(pyridine) components.²⁴ Thus, an examination of the structural features found in 4 may not only offer fundamental insight into halogen bonding preferences but also suggest additional approaches for influencing the solid state assembly of halo-substituted TPE derivatives.

EXPERIMENTAL SECTION

Haloarene derivatives 6-10 prepared in this study are shown in Scheme 1. Similar experimental procedures were used for each compound as detailed in the representative procedure below.





General Experimental Procedures. Tetraphenol 5^{25} (100 mg, 0.25 mmol) was dissolved in 10 mL THF, and 0.211 mL (1.50 mmol) Et₃N, 3.1 mg (0.025 mmol) DMAP and 4.5 mol equiv of halobenzoyl chloride were added under argon at room temperature. Reactions were maintained for 12 h, and then concentrated in vacuo to afford white solids. The solids were combined with 10 mL 10% aq. NaOH solution and vigorously stirred for 15 min. Stirring was stopped and the solids were allowed to settle at the bottom of the flask and the NaOH solution was decanted. This procedure was repeated twice with 10 mL of H₂O. After the final treatment, the remaining solids were collected by vacuum filtration, washed thoroughly with H₂O, and dried in air. Analytical samples were obtained by recrystallization from pyridine. Solubility issues prevented collection of ¹³C NMR data.

4-Bromo Ester 6. mp > 220 °C. ¹H NMR (DMF- d_7 , 300 MHz): δ 8.06 (d, J = 8.7 Hz, 8H), 7.93 (d, J = 8.4 Hz, 8H), 7.25 (s, 16H).

4-lodo Ester 7. mp > 220 °C. ¹H NMR (DMF- d_7 , 300 MHz): δ 8.06 (d, J = 8.7 Hz, 8H), 7.93 (d, J = 8.4 Hz, 8H), 7.25 (s, 16H). HRMS (ESI⁺): Calcd for C₅₄H₃₂I₄O₈·Na ([M + Na]⁺), 1338.8174; found 1338.8189.

Table 1. Crystallographic Data for 6 and 7

	6•(Py)	7•(Py)	$6 \cdot (DMF)_2$	$7 \cdot (DMF)_2$	7•(Py) ₃
crystallization yield (%)	88	88	81	88	79
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P2_1/n$
a/Å	10.543(4)	10.6242(12)	10.2173(11)	10.2230(11)	10.3097(11)
b/Å	16.296(5)	16.3746(17)	16.4911(17)	16.4842(17)	37.511(4)
c/Å	17.040(6)	16.9432(18)	19.045(2)	19.0391(19)	16.7490(18)
$\alpha/^{\circ}$	112.180(16)	111.993(5)	65.831(5)	65.799(5)	90
$\beta/^{\circ}$	90.699(15)	91.015(5)	85.161(5)	85.211(5)	107.176(5)
$\gamma/^{\circ}$	106.481(19)	106.380(5)	73.224(5)	73.177(5)	90
$V/Å^3$	2576.0(16)	2596.8(5)	2801.0(5)	2798.9(5)	6188.4(11)
Ζ	2	2	2	2	4
$D_{ m calc}$	1.534	1.775	1.439	1.698	1.663
$\mu \ (\mathrm{mm}^{-1})$	3.180	2.456	2.928	2.284	2.072
T/K	210(2)	200(2)	190(2)	200(2)	190(2)
no. of reflns	12376	27748	33797	40387	69935
no. of unique reflns	3814	8664	7279	7290	11341
no. of reflns with $I > 2\sigma(I)$	2715	6397	5250	4182	6764
no. of params	202	650	687	666	714
$R_1 \left[I > 2\sigma(I) \right]$	0.1273	0.0523	0.0748	0.0589	0.0499
wR ₂	0.3879	0.1189	0.2400	0.1335	0.1047

Table 2. Crystallographic Data for 8-10

	8·(DMF)	8·(Py)	9	10
crystallization yield (%)	81	81	80	87
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\overline{1}$	$P2_1/n$	$P\overline{1}$
a/Å	11.3913(12)	11.9174(13)	22.073(3)	10.2588(11)
b/Å	14.9677(16)	15.3574(16)	8.6817(10)	15.3024(16)
c/Å	29.896(3)	16.0001(17)	23.886(3)	30.704(4)
$\alpha/^{\circ}$	90	65.224(5)	90	96.614(5)
$\beta/^{\circ}$	93.341(5)	70.717(5)	94.603(5)	90.414(5)
$\gamma/^{\circ}$	90	77.858(5)	90	95.087(5)
$V/Å^3$	5088.7(9)	2500.8(5)	4562.5(10)	4768.4(9)
Ζ	4	2	4	4
D_{calc}	1.568	1.604	1.643	1.834
$\mu \ (\mathrm{mm}^{-1})$	3.222	3.277	3.586	2.669
T/K	190(2)	190(2)	190(2)	190(2)
no. of reflns	45136	29682	54032	46871
no. of unique reflns	6649	8967	5974	16697
no. of reflns with $I > 2\sigma(I)$	4033	5412	3415	8161
no. of params	642	677	595	1189
$R_1 \left[I > 2\sigma(I) \right]$	0.0519	0.0478	0.0597	0.0563
wR ₂	0.1124	0.0886	0.1178	0.0938

3-Bromo Ester 8. mp > 220 °C. ¹H NMR (DMF- d_7 , 300 MHz): δ 8.28 (s, 4H), 8.17 (d, J = 8.1 Hz, 4H), 7.98 (d, J = 8.1 Hz, 4H), 7.62 (t, J = 7.95 Hz, 4H), 7.28 (s, 16H). HRMS (ESI⁺) Calcd for C₅₄H₃₂Br₄O₈·Na ([M + Na]⁺), 1148.8708; found, 1148.8710.

2-Bromo Ester 9. mp > 220 °C. ¹H NMR (DMF- d_7 , 300 MHz): δ 8.08 (m, 4H), 8.02 (m, 4H) 7.86 (m, 4H), 7.61 (m, 4H), 7.29 (s, 16H). HRMS (EI) Calcd for C₅₄H₃₂Br₄O₈ ([M⁺]), 1123.8831; found, 1123.8840.

2-lodo Ester 10. mp > 220 °C. ¹H NMR (DMF- d_7 , 300 MHz): δ 8.15 (m, 4H), 8.04 (m, 4H), 7.82 (m, 4H), 7.63 (m, 4H), 7.29 (s, 16H). HRMS (ESI⁺) Calcd for $C_{54}H_{32}I_4O_8$ ·Na ([M + Na]⁺), 1338.8174; found 1338.8182.

X-ray Crystallography. Single crystals of 6-10 were grown by slow evaporation of solutions prepared by dissolving 15 mg of compound in 1 mL of either DMF or pyridine. Crystallization yields are given in Tables 1 and 2. Bulk sample homogeneity of $6 \cdot (DMF)_2$, $7 \cdot (DMF)_2$, $8 \cdot (py)$, $8 \cdot (DMF)$, and 9 was confirmed by comparison of calculated and measured powder X-ray diffraction (PXRD) patterns.

The remaining crystalline samples proved too fragile for PXRD analysis and rapid transformation to amorphous material was observed upon removal from their respective mother liquors. Diffraction data were collected on a Nonius-Kappa CCD diffractometer. Crystallographic data are shown in Tables 1 and 2. Selected details concerning structure solution and refinement are described below and full details can be found in the Supporting Information (CIF).

6•(**py**). A partially occupied pyridine solvate is included in the structure (occ = 0.78(4)). The pyridine was modeled as a rigid group (C(N)–C = 1.39 Å, C(N)–C(N)–C = 120°) with isotropic displacement parameters. Data above 40% 2 theta were excluded from the final cycles of refinement as few (<10%) were above background levels. Comparison of the final F^2 (obs) vs F^2 (calc) indicated that the crystal was a non-merohedral twin. Attempts to determine the twin law were not successful. Because of the limited data set phenyl rings were modeled as rigid groups and only the Br atoms were modeled with anisotropic displacement parameters.

6·(**DMF**)₂. The structure contains two sites partially occupied by DMF solvates. One site (O81–C83) refined to 0.626(12) occupancy while the other site (O91–C93) refined to 0.546(14) occupancy. The two sites were restrained to have the same conformation. The anisotropic displacement parameters were restrained with the rigid bond restraint. A comparison of F^2 (obs) with F^2 (calc) indicated the existence of non-merohedral twinning but attempts to identify the (probably rotational) twinning proved unsatisfactory.

7·(py). The pyridine solvate in this structure was refined to 0.910(13) occupancy.

7•(**DMF**)₂. The two DMF solvates were refined to have occupancies of 0.822(13) (O81–C83) and 0.751(14) (O91–C93). Both molecules were restrained to have the same conformations. The higher occupancy site was refined with anisotropic displacement parameters, while the other site was refined with isotropic displacement parameters.

7·(**py**)₃. Three pyridine solvates were identified in this structure. Two pyridines refined to occupancy = 1.000 and were not disordered. The third pyridine (C91–C96) was disordered over three sites. These disordered sites were restrained to sum 1.000 and converged to give partial occupancies of 0.433(16), 0.280(11), and 0.261(17). Each pyridine was modeled as a rigid group (C(N)–C = 1.39 Å, C(N)– C(N)–C = 120°).

8 (py). One bromobenzoate group in this structure was disordered via ~180° rotation about the C64–O67 bond. The disorder refined to 0.9185(17)/0.0915(17). The phenyl ring was modeled as a rigid group, and the minor site benzoate was restrained to be flat and have the same bond distances as the major site. All non-hydrogen atoms were assigned the same isotropic displacement parameters. The pyridine solvate molecule was also disordered over two sites (0.888(5)/0.111(5)). The minor site was refined as a rigid group $(C(N)-C = 1.39 \text{ Å}, C(N)-C(N)-C = 120^\circ)$ and assigned the same isotropic displacement parameters.

RESULTS AND DISCUSSION

While tetraphenylethylenes 6-10 were easily prepared via acylation of tetraphenol 5, all compounds proved to be sparingly soluble in common organic solvents. This characteristic initially hampered efforts to grow X-ray quality single crystals. Eventually, we found that dissolution of the haloarene substrates in warm DMF or pyridine followed by slow evaporation over 1-5 days was an effective crystallization procedure, and single crystals of 6-8 were obtained from each of these solvents as solvent-inclusion complexes. Crystals of *ortho*-halobenzoate esters 9 and 10 were obtained from DMF as close-packed materials.

The inclusion complexes $6 \cdot (py)$ and $7 \cdot (py)$ obtained from slow evaporation of pyridine solutions were found to be virtually isostructural. In each case, TPE molecules adopt propeller-like conformations typical of tetraphenylethylenes in the solid state.¹⁵ Individual molecules of 6/7 are engaged in two types of halogen bonding interactions resulting in formation of one-dimensional (1D) chains. As shown in Figure 1, these chain motifs are mediated by complementary $X \cdots O = C$ and $X \cdots \pi$ halogen bonding (see Figure 1 caption for relevant distances and angles). In the case of the halogen $-\pi$ contacts, the closest X··· π_{arene} interaction is to the midpoint of an arene π bond rather than the arene centroid.²⁶ One-dimensional chains are extended into two-dimensional (2D) layers via a combination of arene edge-to-face interactions between adjacent halobenzoyl moieties and additional X··· π (over bond) contacts as shown in Figure 1c. Disordered pyridine solvate molecules are housed within cavities formed at the chain-chain interface. While there is considerable precedent for pyridyl N···X (especially X = I) halogen bonds,¹ pyridine solvates appear to be serving a spacefilling role in these structures and are not involved in halogen bonding interactions.



Figure 1. (a) 1D chains present in 6·(py). Br···O=C = 3.302 Å, Br··· π_{bond} = 3.623 Å, C–Br···O = 166.22°, C–Br··· π_{bond} = 141.05°. (b) 1D chains in 7·(py). I···O=C = 3.401 Å, I··· π_{bond} = 3.574 Å, C–I···O = 163.68°, C–I··· π_{bond} = 142.88°. (c) View of 2D layers formed from interdigitation of 1D chains along with pyridine solvate molecule in 7·(py). Individual chains are color-coded. Edge-to-face arene interactions and additional interchain I··· π_{bond} interactions (d = 3.718 Å) indicated by black lines. Similar 2D layers are found in 6·(py).

While halogen bonding appears to play an important role in the 2D organization of $6 \cdot (py)$ and $7 \cdot (py)$, stacking of individual layers in the third dimension is mediated by an extensive network of edge-to-face arene contacts (Figure 2). In these structures 2D layers are stacked parallel to the *a* axis in an *abab* pattern slightly offset along *a*. Arene rings in the TPE core interact with arene rings from adjacent TPE cores, while peripheral halobenzoyl rings interact with peripheral halobenzoyl rings in adjacent layers.

Single crystals of **6** and 7 obtained from slow evaporation of DMF exhibited a similar arrangement of 1D chains organized into 2D sheets with included solvent molecules occupying cavities at the interchain interface. A partial view of the 2D sheet structure found in $7 \cdot (DMF)_2$ is shown in Figure 3a. A linear network of I···O=C and I··· π_{arene} halogen bonding interactions similar to those found in the pyridine solvate described above result in ribbon-like chains of individual molecules. Once again, the I··· π_{arene} interaction involves approach of the I to the midpoint of an arene π bond as indicated in Figure 3a. These ribbon-like chains are then arranged in 2D layers via edge-to-face



Figure 2. (a) View of stacked 2D sheets in $7 \cdot (py)$ perpendicular to the stacking axis. Edge-to-face arene contacts indicated with black lines. (b) View of $7 \cdot (py)$ down *a* showing the relationship between two adjacent layers. Light blue = top layer, violet = bottom layer.



Figure 3. (a) 2D sheets formed by parallel alignment of halogen bonded chains in $7 \cdot (DMF)_2$. Relevant distances and angles: C–I···O 3.522 Å, 126.91°; C–I··· π_{bond} 3.535 Å, 149.56°. (b) View of the partial packing of $7 \cdot (DMF)_2$ (down *a*) with channels occupied by included DMF molecules (blue).

 π -stacking of aromatic rings. Additional polar interactions (C– H…O hydrogen bonding) with DMF solvates appear to further reinforce this layered structure. No halogen bonding interactions between the DMF solvates and the iodoarene moieties are evident. The 2D layers stack parallel to the *a* axis in an *abab* pattern mediated by edge-to-face π -stacking interactions similar to those shown in Figure 2. As a consequence of stacking interactions, individual 2D layers are aligned in a slightly offset fashion. This arrangement produces large rhomboid channels of dimensions ~13 × 7 Å that are filled with included DMF solvates (Figure 3b). The presence of these channels produces a relatively porous network with approximately 41% solvent accessible void space as determined using PLATON calculations.²⁷ The DMF inclusion complex obtained from **6** exhibited a similar overall network architecture with Br…O=C and Br… π_{bond} interactions comparable to those observed in the iodo analogue.

We also attempted to prepare cocrystalline networks using a combination of 7 and various compounds possessing two potential halogen bond acceptor sites (e.g., dimethyl malonate, methyl nicotinate, diethyl maleate, and several bis(pyridine)s). These experiments involved mixing 7 and the cocrystallization agent in DMF or pyridine. While no cocrystals were obtained, a new pyridine inclusion complex of stoichiometry $7 \cdot (py)_3$ was isolated and characterized from slow evaporation of a pyridine solution containing 7 and dimethyl malonate. Unlike the structures discussed above, all four iodoarene groups in $7 \cdot (py)_3$ were engaged in some form of halogen bonding that results in linking each molecule of 7 to five other molecules (Figure 4a). Two iodo groups are involved in distinct I $\cdots \pi_{arene}$ interactions with two different molecules of 7. One of these interactions is to the midpoint of an arene bond (over bond interaction, $d_{I\dots\pi} =$ 3.564 Å, C–I··· π angle = 154.15°), while the other involves interaction between an iodo group and an arene carbon (over carbon π interaction, $d_{I\cdots C\text{-arene}} = 3.649$ Å, C–I···C_{arene} angle = 171.11°).^{26d} One of these iodine atoms also serves as a halogen bond acceptor toward an aryl iodide halogen bond donor from a third molecule of 7 ($d_{I\cdots I} = 3.795$ Å, C–I···I angles = 168.24° and 96.73°). A third iodine participates in a halogen bond to a carbonyl group from a fourth molecule of 7 ($d_{I\dots O} = 3.380$ Å, C–I···O angle = 152.49°). Finally, the fourth iodine substituent functions as a halogen bond donor toward a fifth molecule of 7. Such an extensive array of halogen bonds about the semiflexible TPE derivative produces a nonclose packed three-dimensional (3D) architecture in which the pyridine solvates occupy voids as shown in Figure 4b, and no I---pyridine halogen bonds are present. Thermochemical characterization of $7 \cdot (py)$ and $7 \cdot (py)_3$ could not be performed due to the fragility of the crystals. On the basis of calculated densities, however, it appears that $7 \cdot (py)$ is the more close packed structure. It is certainly possible that the tris(pyridine) inclusion complex represents a metastable state along the path to the mono(pyridine) complex. If so, then the marked differences in lattice architecture would indicate that the 3D network of halogen bonding interactions in $7 \cdot (py)_3$ is supplanted in favor of more edge-to-face arene contacts in $7 \cdot (py)$ (Figure 2).

In order to investigate the effect of substitution pattern on halogen bonding interactions, TPE derivative 8 was prepared and characterized. As was the case with 6, two different inclusion complexes were obtained from slow evaporation of DMF or pyridine solutions. However, very few distinct halogen bonding interactions are evident upon analysis of the resulting crystal structures. In 8·(DMF), only one halogen bond between a bromine and the carbonyl group of DMF is apparent (Figure 5a) with a variety of other intermolecular contacts (e.g., C–H…O, C–H… π , arene edge-to-face, and face-to-face) leading to the generation of sheet-like assemblies as shown in Figure 5b. The structure of 8·(py) is somewhat reminiscent of features found

Article



Figure 4. (a) Halogen bonding interactions linking 7 to five additional molecules observed in $7 \cdot (py)_3$. (b) Extended packing in $7 \cdot (py)_3$ down *c*. Pyridine solvates shown in blue.

in inclusion complexes of 6 and 7 in that 8 assembles to form 2D sheets that stack in an *abab* pattern slightly offset down the a axis (Figure 5c). However, close intermolecular contact between an aryl bromine residue and an arene carbon (over carbon Br \cdots π interaction) provides the only evidence for halogen bonding ($d_{Br...C-arene} = 3.310$ Å, C-Br...C_{arene} angle = 150.48°. In part, the absence of extensive halogen bonding interactions in 8 may stem from the location of the aryl halide substituents at electronically unactivated meta-positions of the benzoate rings. Notably, halobenzoate TPE derivatives that feature halogens at electronically activated 4-positions (6 and 7) and 2-positions (9 and 10, vide infra) exhibit significantly more halogen bonding contacts. Steric factors likely play a role in governing the observed halogen bonding patterns as well, although the conformational flexibility of these TPE esters is envisioned to attenuate this effect.¹⁶

The final set of compounds included in this study features TPE frameworks decorated with ortho-substituted bromo- or iodobenzoyl rings. Once again, crystals of both 9 and 10 could



Figure 5. (a) Halogen bonding interaction between 8 and DMF solvate ($d_{Br...O} = 3.407$ Å, C–Br...O angle = 163.6°). (b) Extended packing in 8 (DMF) down *b*. (c) Extended packing of 8 (py) down *a*.

be obtained from slow evaporation of DMF or pyridine solutions. Within each compound the same crystalline modification was observed irrespective of crystallization solvent. Additionally, each compound was obtained as a close-packed structure without any included solvent. In the structure of 9, two types of halogen bonding appear to be significant. Individual molecules of 9 are organized into 1D ribbons via intermolecular Br…Br halogen bonding (Figure 6a). To achieve close packing, each 1D ribbon is connected in a slightly offset manner to adjacent ribbons via Br… π (over carbon) contacts as illustrated in Figure 6b (along with additional C–H…O



Figure 6. (a) Br…Br halogen bonding in 9. (b) Stacked sheet-like packing reinforced with $Br…\pi$ (over carbon) halogen bonding.

interactions not shown in Figure 6). Thus, one bromine atom in each molecule is engaged in amphiphilic bifurcated halogen bonding by acting as a halogen bond donor (electrophile) toward an arene carbon (over carbon π interaction, 3.510 Å, 164.73°) and a halogen bond acceptor (nucleophile) in an attractive Br…Br interaction. A third bromine from each molecule of 9 is also positioned a short distance (3.340 Å) from an arene π -bond in an adjacent ribbon; however, the C–Br… π angle of 126.48° deviates substantially from the ideal halogen bonding value. The fourth bromine does not appear to participate in any significant intermolecular interactions.

The ortho-iodo analogue **10** adopts a slightly different packing arrangement in which independent parallel ribbons are aligned roughly in the *bc* plane to form undulating sheets. Intermolecular interactions within each strand consist of multiple C-H···O interactions along with iodine halogen bonding (Figure 7a). In one ribbon, a halogen bond is observed involving an iodine halogen bond donor and an ester carbonyl halogen bond acceptor ($d_{1...O} = 3.322$ Å, C-I···O = 149.53°). The second unique ribbon features a single intermolecular over carbon I··· π interaction ($d_{1...C-\text{arene}} = 3.347$ Å, C-I···C_{-arene} = 156.13°). Undulating sheets are stacked down the *a* axis in an *abab* pattern with additional interlayer over bond and over carbon I··· π contacts as shown in Figure 7b ($d_{1...\pi-\text{bond}} = 3.332$ and $d_{1...C-\text{arene}} = 3.563$ Å, C-I··· π_{bond} angle = 170.40 and C-I···C_{arene} angle = 146.78°).

The substrates examined in this study were designed to probe the interplay between specific types of halogen bonding interactions and molecular structure in similar but electronically distinct systems. Five basic halogen bonding synthons (illustrated schematically in Scheme 2) were observed in the TPE halobenzoyl esters examined. Table 3 provides a summary of the halogen bonding synthons observed in 6-10. Although all structures (with the exception of $7 \cdot (py)_3$) exhibited nominally similar extended packing architectures consisting of stacked 2D layers, consistent trends in halogen bonding as a function of halogen or substitution pattern were generally not observed. Only in the 1:1 solvent inclusion complexes of the 4halobenzoyl esters were similar halogen bonding motifs present irrespective of structure. However, the halogen bonding interactions in $6/7 \cdot (DMF)$ and $6/7 \cdot (py)$ were all confined to the 2D sheet assemblies formed from parallel alignment of 1D ribbons, and extensive arene edge-to-face contacts appear to constitute the dominant solid state interactions in these structures. Given the abundance of π systems in the substrates 6–10, perhaps it is not surprising that halogen... π synthons II



Figure 7. (a) Parallel ribbons that generate 2D sheets in **10** mediated by intermolecular C–H···O, I···C_{arene}, and I···O interactions. (b) View of stacked sheets in **10** (down b) color-coded to highlight *abab* pattern.

Scheme 2. Halogen Bonding Synthons Exhibited in 6-10



and **III** were the most frequently observed halogen bonding motifs, followed by X···O=C synthon I. Somewhat surprisingly, the X···X halogen bonding motif (synthon **IV**) was observed only in one structure. Our previous studies indicated that this type of interaction was common in compounds somewhat similar to 6-10.¹⁵⁻¹⁷ Moreover, in most structures reported here at least one halogen in the tetra(halo) substrate does not exhibit any significant intermolecular close contacts. One must assume that the energetic value gained by engaging all four halogens in some form of halogen bonding is offset by the disruption of

Table 3. Summary of Solid State Halogen Bonding Interactions (Synthons I–V) Observed in TPE Derivatives 6–10

	I	II	III	IV	v
6•(DMF) ₂	+++	+++			
7•(DMF) ₂	+++	+++			
6•(py)	+++	+++			
7•(py)	+++	+++			
7•(py) ₃		+++	+++		+++
8·(DMF)	+++				
8·(py)			+++		
9			+++	+++	+++
10		+++	+++		



Figure 8. Confocal microscope image of 7.(py).

other weak noncovalent associations (e.g., C–H…O hydrogen bonding, edge-to-face π bonding). In this context, it may be interesting to probe the effect of systematically increasing the halogen bond donor ability of the halide substituents (e.g., through preparation of fluorinated and partially fluorinated bromo/iodo benzyol esters) as a means to disrupt the packing patterns observed in **6–10** in favor of additional (stronger) halogen bonding interactions.

Many tetraphenylethylenes exhibit aggregation-induced emission.²⁰ In dilute solutions TPEs are generally nonfluorescent; however, upon addition of a poor solvent aggregation of TPEs occurs resulting in a fluorescence signal. The origin of this optical behavior is believed to reside in restricted intramolecular motions (e.g., aryl bond rotations) of TPE frameworks when in aggregated states. Luminescence of TPEs also extends to the solid state, and this property was qualitatively apparent in crystals of 6-10 when illuminated with a hand-held UV light. Single crystals of 7.(py) were further examined using confocal microscopy, and a representative image is shown in Figure 8. Solution phase aggregation-induced emission of 7 was also probed. A sample of 7 was dissolved in 100% DMF and the fluorescence spectrum was recorded. The change in fluorescence was then monitored as increasing amounts of H_2O were added to the solution (Figure 9). While the solution was initially nonemissive, a relatively weak fluorescence signal centered at ~460 nm was observed at 20% water content. Continued addition of water produced enhanced emission along with a slight red shift in the fluorescence maxima. Haloarene-TPE derivatives 6 and 8-10 exhibited similar fluorescence profiles (see Supporting Information). Thus, use of TPE derivatives in crystal engineering applications may offer a convenient means for construction or luminescent organic and metal-organic frameworks, and studies along these lines are underway.

CONCLUSIONS

This study was designed to assay the importance of specific halogen bonding interactions in structurally related but electronically differentiated tetratopic haloarenes. Substrates 6-10 were prepared from a readily available tetraphenylethylene derivative lacking strong hydrogen bonding groups in order to maximize the influence of halogen bonding interactions. However, only the 4halobenzoyl-substituted compounds 6 and 7 displayed a high correlation between molecular structure and preferred halogen bonding motifs (X···O=C and X··· π). In general, halogen bonding interactions observed in 6-10 appear to reinforce a common stacked-sheet packing motif in cooperation with edge-to-face arene interactions and C-H···O/ π hydrogen bonding. The presence in some crystals of solvates capable of serving as halogen bond acceptors (i.e., pyridine and DMF) did little to disrupt this packing, and no halogen bonds involving included solvates (with the exception of $8 \cdot (DMF)$) were observed. Future studies



Figure 9. Fluorescence spectra of 7 in DMF and DMF/H₂O mixtures (vol%). No fluorescence was observed until water content was 20%. [7] = 23.17 μ M, λ_{ex} = 375 nm.

will examine the ability to attenuate the influence of these latter two noncovalent attractions through the use of TPE derivatives substituted with more potent (more electrophilic) halogen bond donors.

ASSOCIATED CONTENT

Supporting Information

X-ray data with details of refinement procedures (CIF), fluorescence spectra and confocal microscope images of 6-10, calculated and observed PXRD patterns for $6 \cdot (DMF)_2$, $7 \cdot (DMF)_2$, $8 \cdot (py)$, $8 \cdot (DMF)$, and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: 319-335-3805. Fax: 319-335-1270. E-mail: chris-pigge@uiowa.edu.

ACKNOWLEDGMENTS

We thank the Department of Chemistry, University of Iowa, and Dr. Jonas Baltrusaitis for assistance with confocal microscopy. F.C.P. thanks the College of Liberal Arts & Sciences and the Obermann Center for Advanced Studies for sponsorship of a Career Development Award.

REFERENCES

(1) (a) Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo, G. Angew. Chem., Int. Ed. 2008, 47, 6114-6127. (b) Metrangolo, P.; Resnati, G. Science 2008, 321, 918-919. (c) Metrangolo, P.; Resnati, G.; Pilati, T.; Biella, S. Struct. Bonding (Berlin) 2008, 126, 105-136.
(d) Fourmigué, M. Curr. Opin. Solid State Mater. Sci. 2009, 13, 36-45.

(2) (a) Lommerse, J. P. M; Stone, A. J.; Taylor, R.; Allen, F. H. J. Am. Chem. Soc. 1996, 118, 3108–3116. (b) Riley, K. E.; Merz, K. M. Jr. J. Phys. Chem. A 2007, 111, 1688–1694. (c) Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. J. Am. Chem. Soc. 1986, 108, 4308–4314. (d) Cabot, R.; Hunter, C. A. Chem. Commun. 2009, 2005–2007. (e) Politzer, P.; Murray, J. S.; Clark, T. Phys. Chem. Chem. Phys. 2010, 12, 7748–7757. (f) Sarwar, M. G.; Dragisic, B.; Salsberg, L. J.; Gouliaras, C.; Taylor, M. S. J. Am. Chem. Soc. 2010, 132, 1646–1653.

(3) (a) Murray, J. S.; Riley, K. E.; Politzer, P.; Clark, T. Aust. J. Chem. 2010, 63, 1598–1607. (b) Clark, T.; Hennemann, M.; Murray, J.; Politzer, P. J. Mol. Model. 2007, 13, 291–296.

(4) (a) Riley, K. E.; Murray, J. S.; Politzer, P.; Concha, M. C.; Hobza,
P. J. Chem. Theory Comput. 2009, 5, 155–163 and references cited.
(b) Gavezzotti, A. Mol. Phys. 2008, 106, 1473–1485.

(5) (a) Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 16789–16794. (b) Metrangolo, P.; Pilati, T.; Resnati, G. *CrystEngComm* **2006**, *8*, 946.

(6) Sun, A.; Lauher, J. W.; Goroff, N. S. Science 2006, 312, 1030 and references cited.

(7) (a) Rissanen, K. *CrystEngComm* 2008, 10, 1107–1113.
(b) Bertani, R.; Sgarbossa, P.; Venzo, A.; Lelj, F.; Amati, M.; Resnati, G.; Pilati, T.; Metrangolo, P.; Terraneo, G. *Coord. Chem. Rev.* 2010, 254, 677–695.

(8) Bruce, D. W.; Metrangolo, P.; Meyer, F.; Pilati, T.; Präsang, C.; Resnati, G.; Terraneo, G.; Wainwright, S. G.; Whitwood, A. C. *Chem.—Eur. J.* **2010**, *16*, 9511–9524 and references cited.

(9) (a) Fourmigué, M. Struct. Bonding (Berlin) 2008, 126, 181–207.
(b) Fourmigué, M.; Batail, P. Chem. Rev. 2004, 104, 5379–5418.

(10) Hanson, G. R.; Jensen, P.; McMurtrie, J.; Rintoul, L.; Micallef, A. S. Chem.—Eur. J. **2009**, *15*, 4156–4164.

(11) (a) George, S.; Nangia, A.; Lam, C.-K.; Mak, T. C. W.; Nicoud, J.-F. *Chem. Commun.* **2004**, 1202–1203. (b) Cariati, E.; Forni, A.; Biella, S.; Metrangolo, P.; Meyer, F.; Resnati, G.; Righetto, S.; Tordin, E.; Ugo, R. *Chem. Commun.* **2007**, 2590–2592.

(12) Caronna, T.; Liantonio, R.; Logothetis, T. A.; Metrangolo, P.; Pilati, T.; Resnati, G. J. Am. Chem. Soc. **2004**, *126*, 4500–4501.

(13) (a) Mele, A.; Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. J. Am. Chem. Soc. 2005, 127, 14972–14973. (b) Chudzinski, M. G.; McClary, C. A.; Taylor, M. S. J. Am. Chem. Soc. 2011, 133, 10559–10567. (c) Cavallo, G.; Metrangolo, P.; Pilati, T.; Resnati, G.; Sansotera, M.; Terraneo, G. Chem. Soc. Rev. 2010, 39, 3772–3783.

(14) (a) Voth, A. R.; Hays, F. A.; Ho, P. S. Proc. Natl. Acad. Sci. U. S. A. 2007, 104, 6188–6193. (b) Lu, Y.; Shi, T.; Wang, Y.; Yang, H.; Yan, X.; Luo, X.; Jiang, H.; Zhu, W. J. Med. Chem. 2009, 52, 2854–2862 and references cited.

(15) (a) Kumar, V. S. S.; Pigge, F. C.; Rath, N. P. *CrystEngComm* **2004**, *6*, 102–105. (b) Pigge, F. C.; Vangala, V. R.; Swenson, D. C. *Chem. Commun.* **2006**, 2123–2125.

(16) Pigge, F. C.; Vangala, V. R.; Swenson, D. C.; Rath, N. P. Cryst. Growth Des. 2010, 10, 224–231.

(17) Pigge, F. C.; Vangala, V. R.; Kapadia, P. P.; Swenson, D. C.; Rath, N. P. Chem. Commun. **2008**, 4726–4728.

(18) Banerjee, M.; Emond, S. J.; Lindeman, S. V.; Rathore, R. J. Org. Chem. 2007, 72, 8054–8061 and references cited.

(19) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. J. Am. Chem. Soc. **1998**, 120, 6931–6939.

(20) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Chem. Commun. 2009, 4332-4353.

(21) Liu, L.; Zhang, G.; Xiang, J.; Zhang, D.; Zhu, D. Org. Lett. 2008, 10, 4581–4584.

(22) (a) Chen, Q.; Bian, N.; Cao, C.; Qiu, X.-L.; Qi, A.-D.; Han, B.-H. Chem. Commun. 2010, 46, 4067–4069. (b) Liu, Y.; Deng, C.; Tang, L.; Qin, A.; Hu, R.; Sun, J. Z.; Tang, B. Z. J. Am. Chem. Soc. 2011, 133, 660–663. (c) Kato, T.; Kawaguchi, A.; Nagata, K.;

Hatanaka, K. Biochem. Biophys. Res. Commun. 2010, 394, 200–204.

(23) Kapadia, P. P.; Widen, J. C.; Magnus, M. A.; Swenson, D. C.; Pigge, F. C. *Tetrahedron Lett.* **2011**, *52*, 2519–2522.

(24) Kapadia, P. P.; Ditzler, L. R.; Baltrusaitis, J.; Swenson, D. C.; Tivanski, A. V.; Pigge, F. C. J. Am. Chem. Soc. 2011, 133, 8490-8493.

(25) Schultz, A.; Diele, S.; Laschat, S.; Nimtz, M. Adv. Funct. Mater. 2001, 11, 441–446.

(26) (a) Schollmeyer, D.; Shishkin, O. V.; Rühl, T.; Vysotsky, M. O. *CrystEngComm* **2008**, *10*, 715–723. (b) Swierczynski, D.; Luboradzki, R.; Dolgonos, G.; Lipkowski, J.; Schneider, H.-J. *Eur. J. Org. Chem.* **2005**, 1172–1177. (c) Prasanna, M. D.; Guru Row, T. N. *Cryst. Eng.* **2000**, *3*, 135–154. (d) Vasilyev, A. V.; Lindeman, S. V.; Kochi, J. K. *Chem. Commun.* **2001**, 909–910.

(27) Spek, A. L. *PLATON – A Multipurpose Crystallographic Tool;* University of Utrecht: The Netherlands, 1999.