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The synthesis and crystal structures of halogenated tolans *p*-X–C_6H_4–C≡C–C_6F_5 and *p*-X–C_6F_4–C≡C–C_6H_5 (X = F, Cl, Br, I)†

Jonathan C. Collings, Jacquelyn M. Burke, Philip S. Smith, Andrei S. Batsanov, Judith A. K. Howard and Todd B. Marder*

Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: todd.marder@durham.ac.uk; Fax: +44(191)-334-4749; Tel: +44(191)-334-2037

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A series of halogenated, partially fluorinated tolans of general formula *p*-X–C_6H_4–C≡C–C_6F_5 [X = I (**1**), Br (**2**), Cl (**3**), F (**4**)] and *p*-X–C_6F_4–C≡C–C_6H_5 [X = I (**5**), Br (**6**)] have been prepared *via* palladium-catalysed Sonogashira cross-coupling, or for X = Cl (**7**), by nucleophilic aromatic substitution reactions. The single-crystal X-ray structures of **1**–**3** and **5**–**6** have been determined. The structures reveal that the molecular packing is characterized by either arene–perfluoroarene interactions (**3**), or halogen–halogen interactions (isomorphous **1** and **2**), or neither (isomorphous **5** and **6**). The structure of **3** represents the first fully determined crystal structure of a compound that contains a halogen atom other than fluorine, in which arene–perfluoroarene interactions are present.

1. Introduction

The electronic, optical and liquid crystal properties of polymers, oligomers, dendrimers and macrocycles based on the arylene ethynylene motif,[2] have led to interest in smaller arylene ethynylene derivatives such as diphenylethynes (tolans) and 1,4-bis(phenylethynyl)benzenes (BPEBs). In this regard, we have been carrying out a systematic examination of the synthesis, structure and properties of tolans, BPEBs and 9,10-bis(phenylethynyl)anthracenes (BPEAs), substituted with various functional groups at the terminal positions.[3]

Their molecular structures are of particular importance, especially in respect of their planarity. The dihedral angles between the mean planes of the phenyl rings are determined by the rotation about the carbon–carbon single bonds. This in turn depends on the degree of conjugation between the two phenyl rings through the carbon–carbon triple bond. The gas-phase molecular structure of tolan, studied by electron diffraction and electronic spectroscopy in supersonic jets, is consistent with quasi-free ring rotation.[4] However, tolan itself is planar in the solid state.[4a,5] Crystal structures of tolan derivatives reveal a variety of dihedral angles between the arene rings, although most are close to planar.[6] Crystal packing forces are believed to be responsible for the variation in conformations.

Tolans that crystallise in non-centrosymmetric space groups are useful for second harmonic generation (SHG).[7] Recently, non-centrosymmetric crystal structures have been reported for tolans with a terminal alkyne substituent, and these have been shown to have large SHG activities.[8] Another aspect of the crystallography of tolans is polymorphism, one particularly interesting compound in this regard being 4-methoxy-4′-nitrotolan, which exhibits at least three polymorphs depending on the solvent from which it is grown. Although at least two of these polymorphs are centrosymmetric, one polymorph is non-centrosymmetric and is therefore potentially suitable for SHG.[9] Thus, even in dipolar systems, a variety of packing arrangements may be close in energy.

Fluorine substituents are often used to modify the structural, electronic and optical properties of molecules. We have thus begun to synthesise selectively fluorinated tolans and BPEBs and to evaluate their properties.[10] We have recently shown that 1,4-bis(phenylethynyl)tetrafluorobenzene forms a 1:1 complex with 1,4-bis(pentafluorophenylethynyl)benzene,[11] and 1,4-bis(phenylethynyl)benzene forms a 2:1 complex with 1,4-bis(pentafluorophenylethynyl)tetrafluorobenzene.[1] The complexes are stabilized *via* arene–perfluoroarene interactions, which were first discovered when it was found that an equimolar mixture of benzene and hexafluorobenzene (HFB) forms a complex with a melting point *ca.* 20 °C higher than either component.[12] Subsequently, the crystal structures of this and other complexes, containing either HFB or octafluoronaphthalene, have shown them to be composed of infinite stacks of alternating arene and perfluoroarene molecules.[13] The arene–perfluoroarene stacking motif also occurs in the crystal structures of partially fluorinated molecules,[14] as observed in the crystal structure of (phenylethynyl)pentafluorobenzene, which consists of stacks of parallel molecules in a head-to-tail arrangement, and similarly, in the crystal structures of many 4-RO–C_6F_4–C≡C–C_6H_5 compounds.[15]

Fluorine substituents are also used to modify the liquid crystalline (LC) phase behaviour of mesogens. Several fluorinated tolan and BPEB derivatives substituted by terminal alkoxy chains have been observed to exhibit LC phases.[16] Interestingly, our BPEB binary complexes exhibit LC phase behaviour not observed in the pure components, which is postulated to be a result of the arene–perfluoroarene interactions.[1,11]

There are, as yet, no crystal structures featuring arene–perfluoroarene stacking between molecules which contain halogen atoms other than fluorine. Therefore, it is not known what effect, if any, their presence has on the arene–perfluoroarene interaction. Herein we report the synthesis and crystal structures of a series of selectively fluorinated tolans containing one other halogen atom, with the general formulae *p*-X–C_6H_4–C≡C–C_6F_5 [X = I (**1**), Br (**2**), Cl (**3**), F (**4**)] and *p*-X–C_6F_4–C≡C–C_6H_5 [X = I (**5**), Br (**6**), Cl (**7**)] as shown in Scheme 1. Compounds **5**, **6**, and **7** have been reported previously; **7** was prepared by nucleophilic substitution at the *para*-position of chloropentafluorobenzene by lithium phenylacetylide, and **5** and **6** were prepared *via* lithiation at the C–Cl bond of **7**, followed by reaction with iodine and bromine, respectively.[17] However, no experimental details were given for these reactions, and the products were not fully characterized. Additionally, **7** was synthesized by Sonogashira coupling of an aryl triflate,[18] although again, the compound was not fully characterized.

2. Results and discussion

2.1 Synthesis

Cross-coupling reactions were carried out under standard Sonogashira conditions, using a catalyst system composed of

† Arene–Perfluoroarene Interactions in Crystal Engineering, Part 12. For Part 11 see ref. 1.

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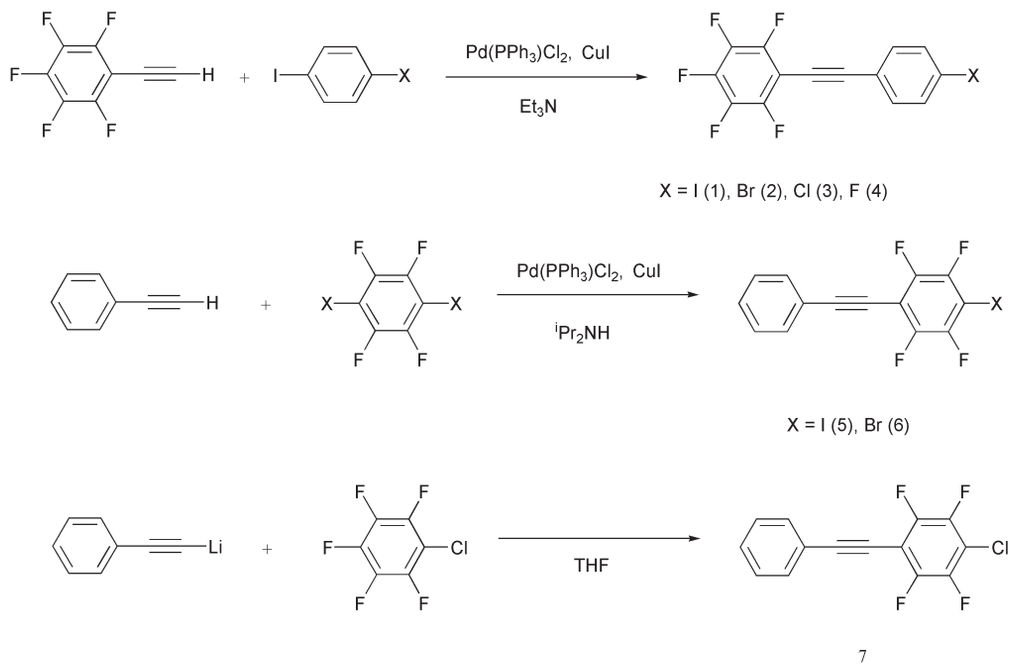

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Scheme 1 The synthesis of **1**–**7**.

$Pd(PPh_3)_2Cl_2$ and CuI, each in 1% molar ratio compared to the aryl halide. A slight excess (1.2 equivalents) of the appropriate phenylacetylene was employed. Some of the reactions took place at room temperature, although several needed some additional heating to proceed to completion. All of the reactions were performed in dry, deoxygenated amine solvents, with triethylamine being used in preference to diisopropylamine for all reactions involving reagents with a pentafluorophenyl group, in order to avoid possible nucleophilic substitution at the *para* position by a secondary amine.[19] The progress of the reactions was monitored by GC-MS, which could also detect the formation of any side-products. In most cases, trace amounts of butadiynes were observed, consistent with them being formed only in the catalyst initiation step.[3a]

The 1-halogeno-4-(pentafluorophenylethynyl)benzenes (**1**–**4**) were prepared (Scheme 1) by the coupling of pentafluorophenylacetylene with the appropriate aryl halide. Pentafluorophenylacetylene can be obtained in respectable yields from the base-induced hydrodesilation of its trimethylsilylated precursor, which is, in turn, obtained from the Sonogashira cross-coupling of trimethylsilylacetylene (TMSA) to iodopentafluorobenzene.[20] For the synthesis of **1**, a threefold excess of 1,4-diiodobenzene was used relative to pentafluorophenylacetylene, in order to minimize the formation of 1,4-bis(pentafluorophenylethynyl)-benzene, arising from coupling at both iodo positions. A similar strategy was employed previously in the synthesis of 1-iodo-4-(phenylethynyl)benzene.[21] The product was separated from unreacted 1,4-diiodobenzene and 1,4-bis(pentafluorophenylethynyl)benzene, and much of the diiodobenzene was recovered, by column chromatography and recrystallisation, although the yield was very low. This can be attributed to the electron-withdrawing nature of the pentafluorophenylethynyl moiety which therefore serves as an activating group. This makes the product more susceptible to further coupling, resulting in an increased amount of 1,4-bis(pentafluorophenylethynyl)benzene, and a decreased yield of product.

The synthesis of compounds **2**–**4** was more straightforward, as the bromo-, chloro-, and fluoro- groups present did not undergo coupling to pentafluorophenylacetylene under the reaction conditions. Therefore, an excess of the aryl halide starting material was not required, no significant amounts of side products were generated, and purification required only recrystallisation in order to obtain analytically pure samples in good yields.

The synthesis of **5** and **6** was achieved by the coupling of 1,4-diiodotetrafluorobenzene and 1,4-dibromotetrafluorobenzene respectively to phenylacetylene. Here, as in the synthesis of **1**, a three-fold excess of the dihalogenotetrafluorobenzene was used for similar reasons to those outlined above, and the products were separated from the remaining starting materials by column chromatography. However, these reactions gave respectable yields of product with only small amounts of 1,4-(phenylethynyl)tetrafluorobenzene being produced, which is probably due to the products being less reactive towards further coupling than the starting material because of the phenylethynyl group being a weaker electron acceptor than the pentafluorophenylethynyl group.

It was initially decided to attempt the synthesis of compound **7** analogously by cross-coupling phenylacetylene to 1-bromo-4-chlorotetrafluorobenzene. However, the resulting reaction was shown by GC-MS to produce a mixture of **7** and 4-phenylethynyl-2,3,5,6-tetrafluorobenzene, arising from hydrodehalogenation of the chloro group. Hydrodehalogenation has been observed previously in these cross-couplings,[3a] and seems to be particularly prevalent for highly fluorinated aryl halides. As the side-product was not easily separated from the product by either column chromatography or recrystallisation, it was decided to resort to the original method[16] of adding chloropentafluorobenzene to lithium phenylacetylide at low temperature. This produced a clean product although the yield was rather low.

2.2 Crystal structures

The structures of compounds **1**, **2**, **3**, **5** and **6** were determined from single-crystal X-ray diffraction data collected at 100–120 K (Table 1); we could not obtain satisfactory crystals of compounds **4** and **7**. Each structure contains one molecule per asymmetric unit, shown in Fig. 1. In molecule **3**, the two benzene rings form a dihedral angle (τ in Table 2) of 3.4°, similar to 4.8° in $PhC{\equiv}CC_6F_5$.[15] In the other four compounds the twist is larger, τ = 9.4 to 15.7°. Unlike $PhC{\equiv}CC_6F_5$ and tolan itself, molecules **1**–**3** also show a substantial deviation from linearity, as indicated by the angle (φ in Table 2) between the vectors C(1)···C(4) and C(9)···C(12). Molecules **5** and **6**, however, remain practically linear. The bond distances are unexceptional.

Each structure contains infinite stacks of molecules, running parallel to the crystal axis *y*, and with interplanar separations (*d* in Table 3) characteristic of close contact of aromatic molecules. Nevertheless, these five structures present three different packing motifs, as illustrated by Figs. 2 and 3. The monoclinic

Table 1 Crystal data and structure refinement parameters

Compound	**1**	**2**	**3**	**5**	**6**
Formula	$C_{14}H_4F_5I$	$C_{14}H_4F_5Br$	$C_{14}H_4F_5Cl$	$C_{14}H_5F_4I$	$C_{14}H_5F_4Br$
Formula weight	394.07	347.08	302.62	376.08	329.09
T/K	105(2)	100(2)	110(2)	100(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a/Å	21.417(7)	20.517(1)	6.076(1)	12.668(2)	12.752(1)
b/Å	4.9672(16)	5.181(1)	7.488(1)	5.074(1)	4.966(1)
c/Å	11.692(4)	11.254(1)	13.168(1)	18.833(3)	18.367(1)
α/°	90	90	85.343(1)	90	90
β/°	92.288(5)	96.922(1)	86.054(1)	93.703(4)	93.231(2)
γ/°	90	90	83.332(1)	90	90
V/Å^3	1242.9(7)	1187.6(1)	592.1(1)	1208.1(3)	1161.3(2)
Z	4	4	2	4	4
ρ_{calcd}/g cm^{-3}	2.106	1.941	1.698	2.068	1.882
μ/mm^{-1}	2.62	3.51	0.37	2.68	3.57
Transmission range	0.30–0.88	0.23–0.84	0.81–0.98	0.62–0.78	0.77–1.00
Total reflections	11360	10137	6110	11022	11716
Unique refls.	2850	2697	2698	2769	2548
Refined parameters	181	197	181	172	192
R_{int}	0.052	0.039	0.016	0.039	0.089
R [F, $I > 2\sigma(I)$]	0.053	0.030	0.030	0.027	0.037
wR (F^2, all data)	0.143	0.082	0.088	0.057	0.083

Table 2 Intramolecular parameters

	Bond lengths/Å			Angles/°	
Compound	C(4)–C(7)	C(7)≡C(8)	C(8)–C(9)	τ	φ
1	1.430(8)	1.205(9)	1.420(8)	9.4	6.9
2	1.438(3)	1.203(4)	1.432(3)	15.7	10.6
3	1.433(2)	1.195(2)	1.423(2)	3.4	4.8
5	1.438(4)	1.175(4)	1.446(4)	13.1	1.4
6	1.435(5)	1.191(5)	1.436(5)	12.8	1.4

Table 3 Intermolecular packing parameters[a]

Compound	d/Å	θ/°	ω/°
1	3.43	46.3	87.5
2	3.46	48.1	83.8
3	3.38	25.5	0
5	3.48	46.7	86.5
6	3.38	46.2	87.5

[a] For uniformity, the molecular plane is defined as the mean plane of all carbon atoms, ignoring halogens and H atoms.

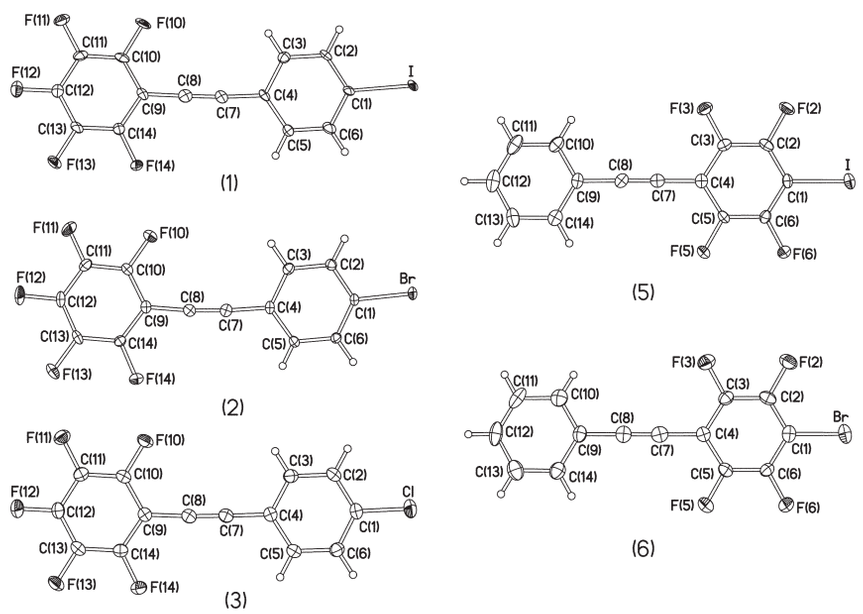

Fig. 1 The molecular structures of **1**, **2**, **3**, **5** and **6** with thermal ellipsoids drawn at 50% probability level.

(space group $P2_1/c$) crystal structures of compounds **1** and **2** are very similar and can be regarded as isomorphous with the bromine–iodine substitution. In the same way, compound **5** is isomorphous with **6**, both crystallising in the monoclinic space group $P2_1/n$. In these four structures, the adjacent molecules in a stack are related by the b translation and therefore are strictly parallel, and all interplanar separations along a stack are symmetrically equivalent. The stack is strongly slanted, as indicated by the 'offset angle' (θ in Table 3) between the direction of the stack and the normal to the molecular planes. The offsets in structures **1**, **2**, **5** and **6** are similar in both magnitude and direction, so that the C≡C bond of each molecule is sandwiched between a C–C bond of a benzene ring on one side and a C–C bond of a fluorinated benzene ring on the other (Fig. 2). Thus, there is no overlap between parallel arene and perfluoroarene rings, which is the structure-defining synthon in practically all molecular arene : perfluoroarene complexes[13] and in most arylene–ethynylene 'rods' containing both fluorinated and non-fluorinated rings.[15]

Although the directions of all stacks in each structure are parallel, the planes of molecules from adjacent stacks are almost perpendicular (dihedral angle ω in Table 3). The inter-stack

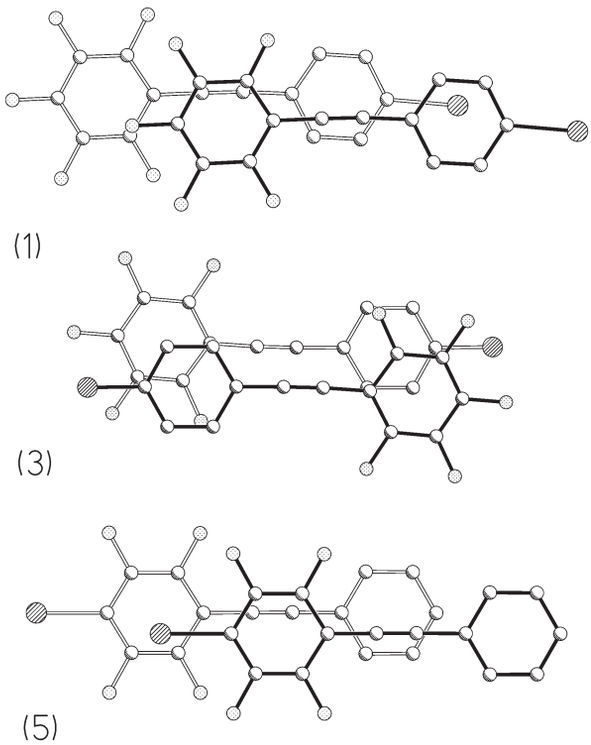

Fig. 2 Overlap of molecules in the stacks for **1** (similar with **2**), **3** and **5** (similar with **6**). H atoms are omitted.

packing motif can be best described as 'flattened herringbone'.[22] In structures **1** and **2** adjacent stacks are related *via* a 2_1 screw axis and their molecules contact head-to-head (Fig. 3), giving rise to an infinite zig-zag chain of (interstack) contacts I···I (3.744 Å) or Br···Br (3.557 Å). These contacts are shorter than twice the (isotropic) van der Waals radii of iodine (4.06 Å) and bromine (3.74 Å), respectively,[23] and have the characteristic "L-shape" of the C–X···X–C moiety, with one C–X···X angle close to 180° (167.4° in **1**, 163.6° in **2**) and the other close to 90° (95.6° in **1** and 85.5° in **2**). In contrast, in structures **5** and **6**, adjacent stacks are related *via* a glide plane and their molecules contact head-to-tail, which precludes any close proximity between iodine or bromine atoms.

Compound **3**, although chemically analogous to **1** and **2**, crystallises in a very different motif: adjacent molecules in a stack are related *via* inversion centres and therefore are antiparallel rather than parallel. The offset angle is much smaller than in **1** and **2** (and also in **5** and **6**). Thus, the structure contains mixed stacks of alternating arene and perfluoroarene rings. Although there are two symmetrically non-equivalent interplanar separations in the stack, in fact they are almost equal. The shortest Cl···Cl separation of 3.927 Å is much greater than twice the van der Waals radius of Cl (3.52 Å), while the contacts Cl···F(11) (x, y, $z-1$) of 3.29 Å and Cl···F(13) ($x-1$, y, $z-1$) of 3.21 Å are close to the sum of van der Waals radii (1.76 + 1.46 = 3.22 Å). The structure being triclinic (space group $P\bar{1}$), molecular planes in adjacent stacks are parallel. In fact, the structure of **3** is isomorphous with that of $PhC{\equiv}CC_6F_5$,with a substitution of one Cl atom for F.[15]

As mentioned previously, co-crystallization of an arene and a perfluoroarene containing one benzene ring or one aromatic condensed system each, always leads to the motif of mixed stacks with alternating arene and perfluoroarene moieties contacting face-to-face (with some offset), although pure components display herring bone motifs without any stacking. The stacking mode is probably due largely to electrostatic interactions.[13c] This motif has also been observed in a number of rod-like molecules containing arene and perfluoroarene groups.[1,11,14a,15] Given that structure **3** displays this 'normal' synthon, one has to explain the absence of this synthon in other structures. A plausible explanation for **1** and **2** seems to be the prevalence of I···I

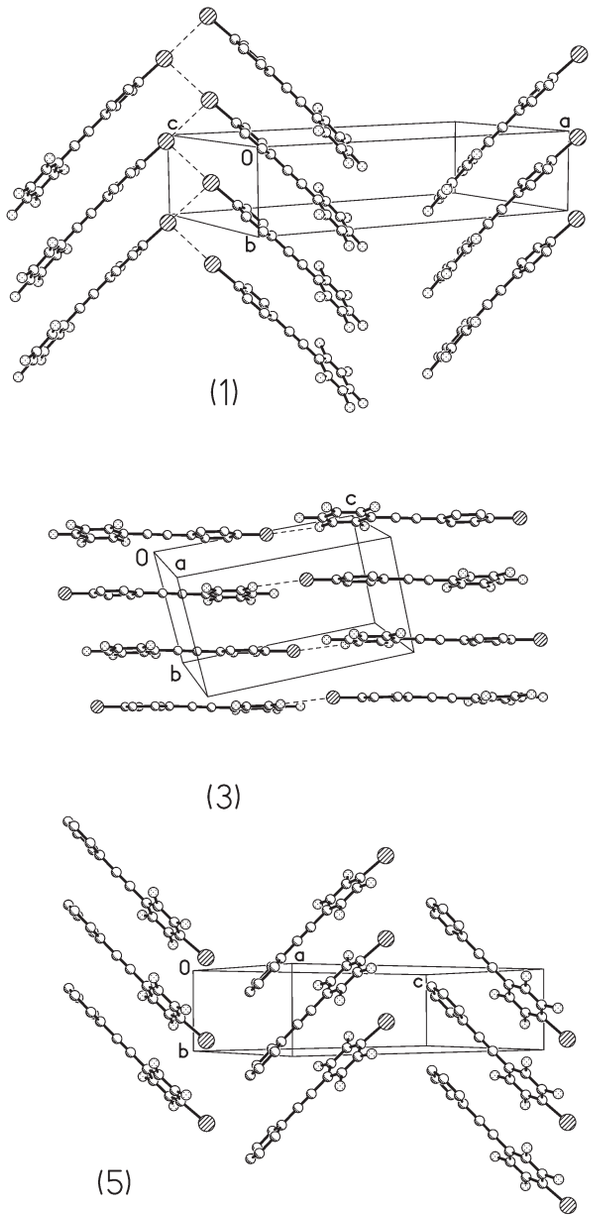

Fig. 3 Crystal packing of **1**, **3** and **5** (H atoms are omitted).

and Br···Br interactions. Short contacts of precisely this type between atoms of halogens (and especially *heavier* halogens) have been known for a long time and often attributed to relatively strong interactions ('secondary bonds', charge-transfer, or quasi-covalent interactions).[24–26] One of the favoured models invokes weak donor–acceptor interactions between the relatively electron-deficient 'polar' part of the halogen atom (close to the continuation of the covalent bond) and electron-rich orbitals normal to this bond. Unfortunately, while structural data on halogen–halogen contacts are abundant, reliable information about the energy and character of the bonding is not. Most of the observed geometrical effects can be rationalised simply by postulating anisotropic shapes of the halogen atoms, flattened at the 'pole' (*i.e.* along the continuation of the covalent bond). The corresponding system of anisotropic van der Waals radii[27] would suggest for **1** and **2** I···I and Br···Br contact distances of *ca.* 3.9 and 3.4 Å, respectively, of which the latter (although not the former) is shorter than the observed distance. A thorough crystallographic and *ab initio* study[28] of Cl···Cl contacts in chlorinated hydrocarbons proved specific *attractive* interactions to be negligible and the van der Waals repulsion anisotropic. Similar work for bromo and iodo derivatives remains to be undertaken, although the higher polarisability of these atoms makes attractive interactions much more likely. Although this

agrees with our present observations (I···I and Br···Br but *not* Cl···Cl interactions supplanting arene–perfluoroarene interactions as the structure-defining factor), more thorough and extensive investigation is obviously necessary, the more so as neither halogen–halogen nor arene–perfluoroarene interactions are realised in structures **5** and **6**.

3. Conclusions

A series of 1-halogeno-4-(pentafluorophenyl–ethynyl)benzenes and 1-halogeno-4-(phenylethynyl)tetrafluorobenzenes have been synthesized. In all but one case this was achieved by palladium-catalyzed Sonogashira cross-coupling. In the case of 1-chloro-4-(pentafluorophenylethynyl)benzene, nucleophilic attack on chloropentafluorobenzene by lithium phenylacetylide was used. The single crystal structures of five of the compounds have been solved from X-ray diffraction data. The molecules show three types of packing motif, one dominated by halogen–halogen interactions, the second dominated by arene–perfluoroarene interactions, and the third in which neither are present. The structure of 1-chloro-4-(pentafluorophenylethynyl)benzene is the first fully determined crystal structure of a compound that contains a halogen atom other than fluorine, in which arene–perfluoroarene interactions are present.

4. Experimental

4.1 Synthesis and characterisation

All reactions were carried out under a dry N_2 atmosphere using standard Schlenk techniques, although once the reactions were complete, further procedures were carried out without any precautions against air. Triethylamine and diisopropylamine were distilled from CaH_2 under N_2 and THF was distilled over Na/benzophenone under N_2, prior to use. All other solvents were GPR grade and used without further purification or drying. Pentafluorophenylacetylene was prepared using a modified literature procedure.[20] The catalyst precursor $Pd(PPh_3)_2Cl_2$ was prepared *via* the literature procedure.[29] All other reagents were obtained from commercial suppliers and used without further purification.

Proton and ^{19}F NMR spectra were recorded on a Varian Mercury spectrometer at 200 MHz and 188 MHz respectively in $CDCl_3$. The chemical shifts are reported in ppm and referenced to the internal standards $SiMe_4$ and $CFCl_3$ respectively. ^{13}C NMR experiments were performed on a Varian spectrometer at 125 MHz with chemical shifts referenced to $SiMe_4$. MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph with a 5971A MSD mass selective ion detector and a 12 m fused silica (5% cross-linked phenylmethylsilicone) capillary column, under the following operating conditions: injector temperature 250 °C, detector temperature 270 °C, the oven temperature was ramped from 70 °C to 270 °C at the rate 20 °C min^{-1}. UHP helium was used as the carrier gas. Elemental analyses were performed using an Exeter Analytical CE-440 analyzer at the University of Durham. Melting points were obtained using a Laboratory Devices Mel-Temp II equipped with a Fluke 51 digital thermometer, and are uncorrected.

1-Iodo-4-(pentafluorophenylethynyl)benzene (1). *Ca.* 300 ml of triethylamine was added to a 500 ml Schlenk flask containing 1,4-diiodobenzene (9.90 g, 30 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol) and CuI (0.02 g, 0.1 mmol). Pentafluorophenylacetylene (2.30 g, 12 mmol) was added dropwise by pipette under N_2 purge and the reaction mixture was stirred for 4 h at 60 °C. The reaction mixture was filtered through a coarse sinter, and then evaporated to dryness *in vacuo.* The crude residue was extracted with hexane, filtered through a 3 cm silica pad, and the filtrate evaporated under reduced pressure. The residue was purified *via* column chromatography on silica with cyclohexane as the eluent, to obtain 5.50 g of recovered 1,4-diodobenzene, and the product, which was re-crystallised from hexane to give colourless plates. Yield: 0.72 g (18%), m.p. 95–96 °C. ^1H NMR (200 MHz): δ 7.74 (m, 2H), 7.29 (m, 2H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −136.2 (m, 2F), −152.5 (m, 1F), −162.0 (m, 2F). $^{13}C\{^1H\}$ NMR (125 MHz): δ 147.1 (d of m, *C*–F, J_{CF} = 250 Hz), 141.5 (d of m, *C*–F, J_{CF} = 255 Hz), 137.8 (d of m, *C*–F, J_{CF} = 250 Hz), 137.7 (*C*–H), 133.2 (*C*–H), 120.9 (C_{ipso} of arene ring), 100.5 (*C*≡C), 100.0 (m, C_{ipso} of fluoroarene ring), 96.0 (*C*–I), 74.4 (*C*≡C). MS (EI) *m*/*z* (rel): 394 (m^+, 100), 266 (10), 248 (10), 217 (10). Anal. Calcd. for $C_{14}H_4F_5I$: C 42.67, H 1.02; Found: C 42.45, H 0.98%.

1-Bromo-4-(pentafluorophenylethynyl)benzene (2). *Ca.* 150 ml of triethylamine was added to a 250 ml Schlenk flask containing 1-bromo-4-iodobenzene (2.82 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol) and CuI (0.02 g, 0.1 mmol). Pentafluorophenylacetylene (2.30 g, 12 mmol) was added dropwise by pipette under N_2 purge. The reaction mixture was stirred for 4 h at room temperature, then filtered through a coarse sinter, and was evaporated to dryness *in vacuo.* The crude residue was extracted with hexane, filtered through a 3 cm thick silica pad, and the filtrate evaporated under reduced pressure. The residue was re-crystallised from hexane to give the pure product as colourless cubes. Yield: 2.80 g (85%), m.p. 103–104 °C. ^1H NMR (200 MHz): δ 7.53 (m, 2H), 7.44 (m, 2H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −136.2 (m, 2F) −152.5 (m, 1F, F) −162.0 (m, 2F, F). $^{13}C\{^1H\}$ NMR (125 MHz): δ 147.1 (d of m, *C*–F, J_{CF} = 252 Hz), 141.5 (d of m, *C*–F, J_{CF} = 254 Hz), 137.7 (d of m, *C*–F, J_{CF} = 250 Hz), 133.2 (*C*–H), 131.9 (*C*–H), 124.2 (*C*–Br), 120.9 (C_{ipso} of arene ring), 100.3 (*C*≡C), 100.0 (m, C_{ipso} of fluoroarene ring), 74.2 (*C*≡C). MS (EI) *m*/*z* (rel): 348 (m+, 94), 346 (100), 266 (74), 248 (82), 247 (39), 241 (22), 240 (30), 217 (79), 216 (36), 173 (26). Anal. Calcd. for $C_{14}H_4F_5Br$: C 48.45, H 1.16; Found: C 48.48, H 1.14%.

1-Chloro-4-(pentafluorophenylethynyl)benzene (3). *Ca.* 50 ml of triethylamine was added to a 100 ml Schlenk flask containing 1-chloro-4-iodobenzene (0.48 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.014 g, 0.02 mmol) and CuI (0.004 g, 0.02 mmol). Pentafluorophenylacetylene (0.46 g, 2.4 mmol) was added by pipette to the mixture under N_2 purge. The reaction mixture was allowed to stir for 3 h at room temperature, and was then heated at 60 °C for 1 h. It was subsequently filtered through a coarse sinter, and then evaporated to dryness *in vacuo.* The crude residue was extracted with hexane, filtered through a 3 cm silica pad, and the filtrate evaporated under reduced pressure. The residue was re-crystallised from hexane to give the product as colourless needles. Yield: 0.46 g (85%), m.p. 99–100 °C. ^1H NMR (200 MHz): δ 7.51 (m, 2H), 7.37 (m, 2H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −136.3 (m, 2F, F), −152.6 (m, 1F, F), −162.0 (m, 2F, F). $^{13}C\{^1H\}$ NMR (125 MHz): δ 147.1 (d of m, *C*–F, J_{CF} = 253 Hz), 141.6 (d of m, *C*–F, J_{CF} = 254 Hz), 137.7 (d of m, *C*–F, J_{CF} = 250 Hz), 135.9 (*C*–Cl), 133.1 (*C*–H), 129.0 (*C*–H), 120.2 (C_{ipso} of arene ring), 100.5 (*C*≡C), 100.2 (m, C_{ipso} of fluoroarene ring), 74.2 (*C*≡C). MS (EI) *m*/*z* (rel): 304 (m+, 31), 302 (100), 266 (15), 248 (21), 217 (19), 216 (12). Anal. Calcd. for $C_{14}H_4F_5Cl$: C 55.54, H 1.32, Found: C 55.56, H 1.24%.

1-Fluoro-4-(pentafluorophenylethynyl)benzene (4). *Ca.* 50 ml of triethylamine was added to a 100 ml Schlenk flask containing 1-fluoro-4-iodobenzene (0.44 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.014 g, 0.02 mmol) and CuI (0.004 g, 0.02 mmol). Pentafluorophenylacetylene (0.46 g, 2.4 mmol) was added by pipette under N_2 purge. The reaction mixture was stirred for 3 h at room temperature, and was then heated at reflux for 2 h. It was then filtered through a coarse sinter, and evaporated to dryness *in vacuo.* The crude residue was extracted with hexane, filtered through a 3 cm silica pad, and the filtrate evaporated under reduced pressure. The residue was re-crystallised from hexane to give the product as colourless crystals. Yield: 0.45 g (79%), m.p. 82–83 °C. ^1H NMR (200 MHz): δ 7.57 (m, 2H), 7.09 (m, 2H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −108.8 (m, 1F), −136.5 (m,

2F), −153.0 (m, 1F), −162.1 (m, 2F). $^{13}C\{^1H\}$ NMR (125 MHz): δ 163.3 (d, *C*–F, J_{CF} = 255 Hz), 147.1 (d, *C*–F, J_{CF} = 255 Hz), 141.5 (d, *C*–F, J_{CF} = 250 Hz), 137.6 (d, *C*–F, J_{CF} = 250 Hz), 134.0 (*C*–H), 117.6 (C_{ipso} of arene ring), 116.0 (m, *C*–H), 100.4 (*C*≡C), 100.1 (m, C_{ipso} of fluoroarene ring), 72.8 (*C*≡C). MS (EI), *m*/*z* (rel): 286 (m+, 100), 266 (7), 255 (11), 235 (9), 217 (8), 216 (8). Anal. Calcd. for $C_{14}H_4F_6$: C 58.74, H 1.40; Found: C 58.87, H 1.42%.

1-Iodo-4-(phenylethynyl)tetrafluorobenzene (5). *Ca.* 300 ml of diisopropylamine was added to a 500 ml Schlenk flask containing 1,4-diiodotetrafluorobenzene (12.06 g, 30 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol) and CuI (0.02 g, 0.1 mmol). Phenylacetylene (1.22 g, 12 mmol) was added dropwise by pipette under a N_2 purge. The reaction mixture was allowed to stir for 4 h. The reaction mixture was filtered through a coarse sinter, and was then evaporated to dryness *in vacuo.* The crude residue was extracted with hexane and filtered through a 3 cm silica silica pad, and the filtrate evaporated under reduced pressure. The residue was purified *via* column chromatography using hexane as the eluent, to obtain 6.40 g of recovered 1,4-diodotetrafluorobenzene, and the product, which was re-crystallised from hexane to give colourless needles. Yield: 2.70 g (72%), m.p. 123–124 °C. ^1H NMR (200 MHz): δ 7.60 (m, 2H), 7.40 (m, 3H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −137.5 (m, 2F), −159.3 (m, 2F). $^{13}C\{^1H\}$ NMR (125 MHz): δ 148.3 (d of m, *C*–F, J_{CF} = 253 Hz), 145.8 (d of m, *C*–F, J_{CF} = 256 Hz), 132.2 (*C*–H), 130.0 (*C*–H), 128.8 (*C*–H), 121.8 (C_{ipso} of arene ring), 102.8 (*C*≡C), 100.3 (m, C_{ipso} of fluoroarene ring), 74.7 (*C*≡C), 73.1 (m, *C*–I). MS (EI), *m*/*z* (rel): 377 (26), 376 (m^+, 100), 248 (11). Anal. Calcd. for $C_{14}H_5F_4I$: C 44.71, H 1.34; Found: C 44.51, H 1.30%.

1-Bromo-4-(phenylethynyl)tetrafluorobenzene (6). *Ca.* 300 ml of diisopropylamine was added to a 500 ml Schlenk flask containing 1,4-dibromotetrafluorobenzene (9.24 g, 30 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol) and CuI (0.02 g, 0.1 mmol). Phenylacetylene (1.22 g, 12 mmol) was added dropwise by pipette under N_2 purge. The reaction mixture was allowed to stir for 4 h, and was then filtered through a coarse sinter, and the filtrate evaporated to dryness *in vacuo.* The crude residue was extracted with hexane, filtered through a 3 cm silica pad, and the filtrate evaporated under reduced pressure. The residue was purified *via* column chromatography using hexane as the eluent, to obtain 4.30 g of recovered 1,4-dibromotetrafluorobenzene, and the product, which was re-crystallised from hexane to give colourless needles. Yield: 2.12 g (65%), m.p. 100–101 °C. ^1H NMR (200 MHz): δ 7.60 (m, 2H), 7.40 (m, 3H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −134.2 (m, 2F), −136.3 (m, 2F). $^{13}C\{^1H\}$ NMR (125 MHz): δ 148.1 (d of m, *C*–F, J_{CF} = 254 Hz), 145.6 (d of m, *C*–F, J_{CF} = 250 Hz), 131.9 (*C*–H), 129.7 (*C*–H), 128.5 (*C*–H), 121.5 (C_{ipso} of arene ring), 102.9 (*C*≡C), 100.3 (m, C_{ipso} of fluoroarene ring), 74.0 (*C*≡C). MS (EI), *m*/*z* (rel): 330 (31), 328 (m^+, 100), 248 (57), 230 (36), 229 (21), 199 (29). Anal. Calcd. for $C_{14}H_5F_4Br$: C 51.17, H 1.52; Found: C 51.32, H 1.54%.

1-Chloro-4-(phenylethynyl)tetrafluorobenzene (7). *Ca.* 50 ml of dry THF was added to a three-necked 250 ml flask equipped with a dropping funnel. Phenylacetylene (1.02 g, 10 mmol) was added *via* pipette to the flask under N_2 purge. A 6.5 ml aliquot of a 1.6 M solution of n-butyllithium in hexanes was added *via* cannula to the dropping funnel under nitrogen. The butyllithium solution was then added dropwise to the reaction mixture at −78 °C, and the reaction was stirred for 1 h. Chloropentafluorobenzene (2.02 g, 10 mmol) was added under nitrogen purge. The mixture was allowed to warm to room temperature, and was observed to darken progressively. After 24 h, the reaction mixture was filtered through a 3 cm silica pad with diethyl ether, and the filtrate was evaporated under reduced pressure to leave a dark residue. The residue was extracted with hexane and filtered through a 3 cm thick silica pad. The filtrate was evaporated under reduced pressure to leave a white residue, which was re-crystallised from hexane to give the product as a white powder. Yield: 1.04 g (37%), m.p. 95–96 °C. ^1H NMR (200 MHz): δ 7.59 (m, 2H), 7.38 (m, 3H). $^{19}F\{^1H\}$ NMR (188 MHz): δ −136.3 (m, 2F), −141.7 (m, 2F). MS (EI) *m*/*z* (rel): 286 (m^+, 33), 285 (16), 284 (100), 248 (10). Anal. Calcd. for $C_{14}H_5F_4Cl$: C 58.93, H 1.91; Found: C 58.76, H 1.56%.

4.2 Crystallography

Diffraction quality crystals were obtained by re-crystallisation from n-hexane or by slow evaporation of dichloromethane solutions. X-Ray diffraction experiments were carried out on Bruker 3-circle diffractometers equipped with a SMART 1000 or (for **6**) SMART 6000 CCD area detector, using graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å). The low temperature of the crystals was maintained using Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. Several runs of narrow (0.3°) ω scans covered the full sphere of the reciprocal space to 2θ = 55° (for **6**, 2θ = 54°). Reflection intensities were corrected for absorption by a semi-empirical method based on multiple scans of identical reflections and Laue equivalents.[30] The structures were solved by direct methods, and refined by full-matrix least squares on F^2 of all the data, using SHELXTL software.[31] Non-H atoms were refined in anisotropic approximation, H atoms were refined in isotropic approximation (in **2** and **6**) or treated as 'riding' in idealised positions. The crystal data and experiment details are listed in Table 1.

CCDC reference numbers 245721–245725. See http://www.rsc.org/suppdata/ob/b4/b411191e/ for crystallographic data in .cif or other electronic format.

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