Effect of alkyl chain length and linker atom on the crystal packing in 6,12-dialkoxy- and 6,12-dialkylsulfanyl-benzo[1,2-*b*:4,5-*b*']*bis*[b]benzothiophenes

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ABSTRACT: The effect of varying the chain length on the solid state conformation and packing of 6,12-dialkoxy- and 6,12-dialkylsulfanyl-benzo[1,2-*b*:4,5-*b*']*bis*[b]benzothiophenes has been studied. The compounds were prepared by $S_N Ar$ reaction of 6,12-difluorbenzo[1,2-*b*:4,5-*b*']*bis*[b]benzothiophene with alkoxides or alkanethiolates derived from C7-C10 alcohols and alkanethiols. Single crystal X-ray diffraction analysis revealed all but two compounds to crystallise in the triclinic space group $P^{-}1$. Two compounds were obtained as monoclinic crystals with space group $P2_1/c$. The alkoxy substituted compounds adopted a molecular conformation with a step from the core and a gauche conformation about the C1'-C2' bond placing the alkyl chains close to parallel with the pentacyclic arene ring system, whereas in the alkylsufanyl derivatives, the alkyl chains were arranged strongly deviated from the plane of the ring, with the sulfur atom anti-periplanar to C3' of the alkyl chain. NMR measurement of T1 relaxation in $CDCl_3$ showed both the alkoxy and alkylsulfanyl substituents to be freely rotating at ambient temperature in solution indicating the orientation of the chains in the solid state was due to packing interactions during crystallization.

INTRODUCTION

Among π-conjugated aromatic materials the benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene ring system has proved particularly useful and demonstrates excellent properties for organoelectronic applications.[1] Due to its high carrier mobility,[2] it has found application in OFETs,[3] OLEDs,[4] self-assembled nano-ribbons,[5] single micro-wire transistors,[6] and solar cells,[7] as well as being employed as a structural unit in MOFs,[8] and in molecular metamorphosis[9,10] to generate other heterocyclic systems such as carbazoles.

Due to the low solubility of many large arene systems, processing the compounds into functional devices is often difficult and such compounds are frequently decorated with alkyl[11] or fluoroalkyl[12] chains to impart organic solubility. The effect of these groups on the solid-state structure after removal of solvent can be critical in determining the alignment of the arene core which is vital to the performance of the device. Alkyl substituents have been used to control the polymerisation of ureas,[13] in the design of molecular rotors,[14] for facilitating thermotropic liquid crystalline behavior,[15] and controlling backbone planarity of semiconducting polymers.[16]

Due to the importance of the benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene in materials science we decided to investigate the solid state structure of derivatives bearing varying alkyl chain lengths (C7-C10) attached by oxygen or sulfur linking atoms to gain insight into the packing arrangement and orientation of alkyl substituents. 6,12-Disubstituted compounds were readily synthesised through substitution of the fluorines in difluorobenzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene **2** by a straightforward S_NAr approach.

EXPERIMENTAL SECTION

Synthesis. Compounds **3a-d**, **4a-d** and **5** were prepared by S_NAr reaction of **2** with the appropriate C7-C10 alkanol, or alkanethiol, in the presence of sodium hydride in DMF or DMSO. Full experimental methods and spectroscopic characterisation data are given in the SI.

Single-Crystal X-ray Diffraction.

Diffraction data were collected on a Bruker SMART APEX 2 CCD diffractometer with Mo-Kα radiation or at the Advanced Light Source Station 11.3.1 using a Bruker D8 diffractometer with a Photon 100 detector and silicon 111-monchromated synchrotron radiation.[17] Data were corrected for Lp effects and for absorption. The structures were solved (by direct methods[18] or via a dual-space charge flipping algorithm[19]) and refined[20] routinely except as follows. For **4a** there were two morphologies of crystal. There were many laths, and far fewer, larger, square plates. Both had the same unit cell parameters and the laths were used for the data collection. For **5** there are two very similar molecules in the asymmetric unit. Coordinates and isotropic displacement

parameters were refined for H atoms in **3a**, **3b** {except U_{iso} 1.2 times that of the carrier C atom for H(10A) and H(10B) only}, **3c**, **4a**, and **5** {except constrained coordinates refinement and U_{iso} 1.2 (1.5 for methyl) times that of the carrier C atoms for H(24A-26A, 45A-52A), H(24B-26B, 45B-52B), and H(26C & 52C) only}. H atoms were refined using the described constraints for **3d**, and **4b-d**. Further details are given in Tables 2 and 3. CCDC 1906520-1906528 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Survey of CSD. A survey of the CSD was conducted (April 2019) using ConQuest (version 1.21).[21] Only four examples of 6,12-disubstituted benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene, bearing alkyl groups at the 6,12-positions were found, and no heteroatom linked groups were reported. Fused benzenoid compounds bearing at least one alkoxy or alkylsulfanyl chain with four or more carbons were therefore examined for comparison with compounds **3** and **4**.

NMR Spectroscopy ^{1}H spectra were recorded at 400 or 500 MHz on Jeol ECS-400 MHz, or Bruker Avance-I 500 MHz instruments in $CDCl_3$. ^{13}C NMR were recorded at 100 or 125 MHz on the same instruments. Spectra were referenced to the residual $CHCl_3$ signal.

RESULTS AND DISCUSSION

Synthesis. Benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophenes have been synthesised by a range of methods including cyclodehydration of *o*-methylsulfinyl biaryls,[3] Bergman cycloaromatisation,[22] dual palladium catalysed C-H activation of diarylsulfides,[23] copper catalyzed sulfuration of 2,2'-diiodo biaryls,[24] double S-arylation of thioacetate with dibenziodolium triflates,[25] and metal free carbocyclative dimerisations.[26] We have described a convenient two-step synthesis of the 6,12-difluoro derivative **2**,[27] while a benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene containing fluorine in the terminal arene rings has also been reported.[23] We now report the synthesis and crystal structures of four 6,12-dialkoxy, and four 6,12-dialkylsulfanyl, benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophenes with alkyl chains ranging from heptyl, C_7 – decyl, C_{10}. The required 6,12-difluorobenzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene **2** was

prepared by a tandem lithiation/ring closure reaction of the *bis*-sulfide **1** (Scheme 1), which is in turn readily prepared from hexafluorobenzene and 2-bromothiophenol.[27]
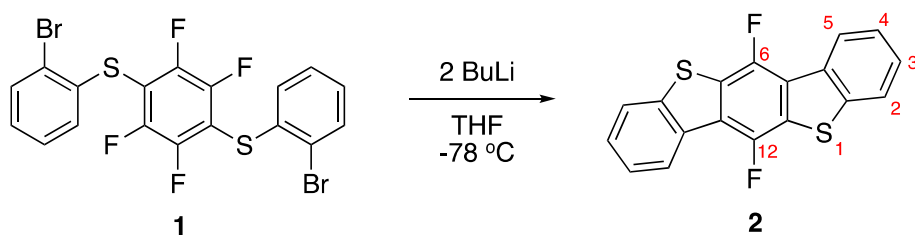
Scheme 1: Synthesis of 6,12-difluorobenzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene **2**.

The two fluorine atoms remaining in the hetarene **2** after the ring closure reaction were found to be susceptible to S_NAr reaction by alkoxide or alkylthiolate anions. Compounds **3a-d** were prepared in moderate to good yield (64, 46, 35, 53% respectively after purification) on treating **2** with the appropriate alcohol in the presence of sodium hydride. DMF or DMSO were found to be suitable solvents, and the reaction proceeded at moderate temperature, typically 65 or 80 °C.
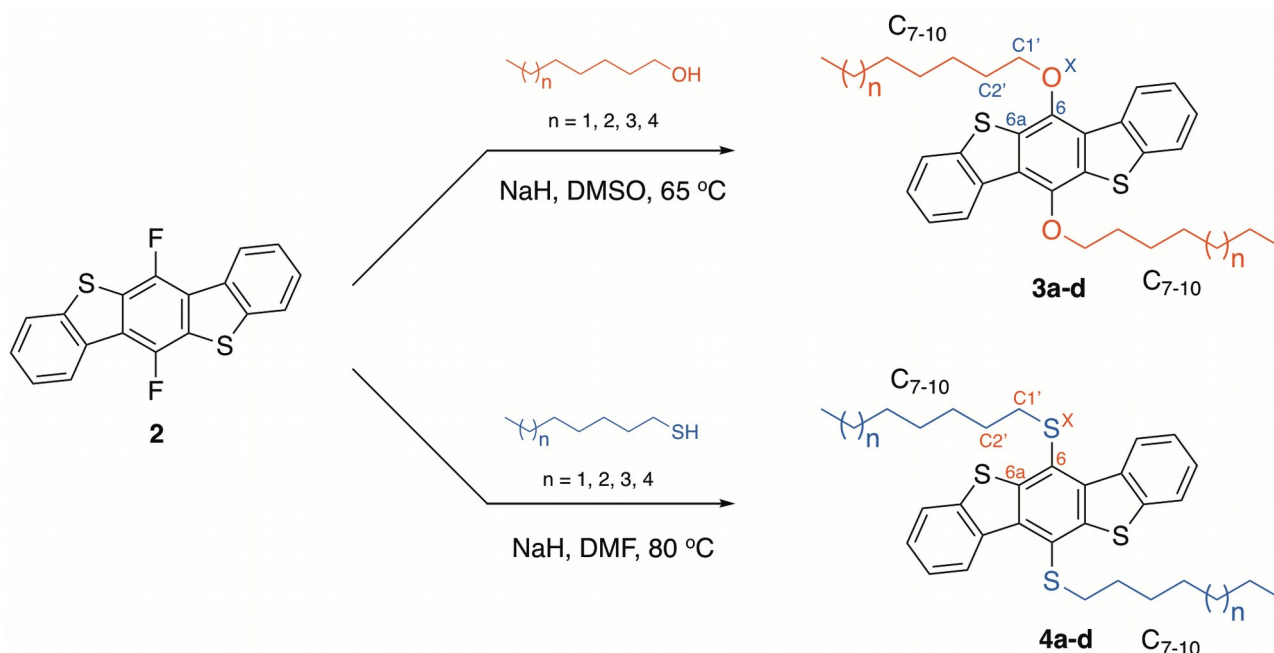
Scheme 2: S_NAr reaction of **2** with alkoxides and alkanethiolates; **a-d** corresponds to C_7-C_{10} chain lengths.

The substitution reaction was best conducted with four equivalents of the alcohol nucleophile. When the reaction was conducted using 1-octanol in the stoichiometric ratio of 1:2 the monosubstitution product **5** (Figure 1) was isolated instead of **3b**. The alkylsulfanyl derivatives **4a**-**4b** were similarly prepared using alkanethiols (heptane – decanethiol) and sodium hydride as base in DMF at 80 °C. The yields after purification were 32, 42, 80 and 58% respectively for **4a**-**4d**.
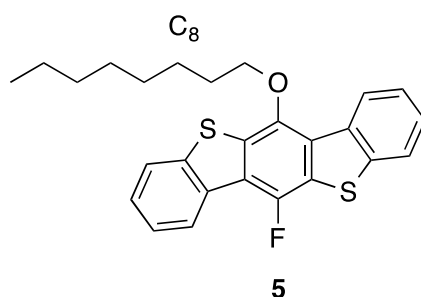

5

Figure 1: Mono-substitution product bearing a single octyl side-chain.

A 1:4 ratio of **2**:RSH was also found optimum, although, due to the higher nucleophilicity of thiolates, the amount of octanethiol needed to form compound **4b** could be reduced from 4 to 2.6 equivalents still affording the disubstitution product in a moderate 46% yield.

Surprisingly however, we were unable to displace the fluorine atoms in **2** with amines or any nitrogen-based nucleophiles. Heating 6,12-difluorobenzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene **2** with neat heptylamine at 150 °C, or under microwave conditions, failed to give the expected diheptylamino derivative **6** (Scheme 3). Similarly, **2** was resistant to sulfonamide anions, sodium azide or hydrazine when subjected to increasingly severe reaction conditions, and **2** was recovered unchanged in all cases. The reason for the lack of reaction with nitrogen nucleophiles, but ready reaction with oxygen and sulfur-based nucleophiles is not clear and is under further investigation.
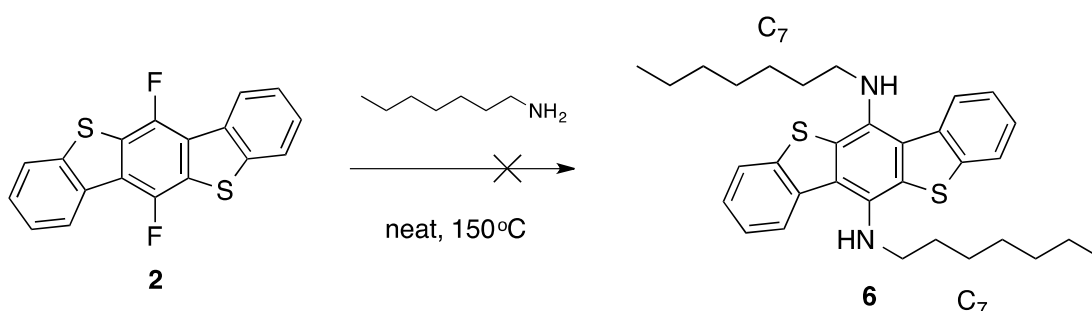
Scheme 3: Attempted reaction of **2** with heptylamine.

Structural Analysis. All the reactions gave solid products which could be crystallized from ethanol. The alkoxy derivatives **3a**-**d** exhibited melting points in the range 60-94 °C while the alkylsulfanyl compounds **4a**-**d** had higher melting points in the range 104-114 °C. At first sight there was no clear correlation between melting point and substituent chain length. However, considering odd and even chain length compounds as separate sets yields a clearer trend. For the alkoxy compounds, the melting point decreased by *ca*. 13 °C on going from a chain length of 7 to 9 and by *ca*. 30 °C on going from 8 to 10. For the alkylsulfanyl compounds there is a much smaller reduction in melting point by *ca*. 2 °C on going from a chain length of 7 to 9, but no change on going from 8 to 10. Thus the alkoxy compounds exhibit far greater melting point variation with chain length than do the alkylsulfanyl compounds.

Compound	Linking atom, O/S	Chain length	Melting point / °C (from ethanol)
3a	O	7	72-74
3b	O	8	93-94
3c	O	9	60-61
3d	O	10	62-63
4a	S	7	112-114
4b	S	8	104-105
4c	S	9	110-113
4d	S	10	104-105*
5	O	8	82-85

Table 1: Melting points of 6,12-dialkoxy- and 6,12-alkylsulfanyl-benzo[1,2-b:4,5-b']*bis*[b]benzothiophenes, and monoalkoxy derivative **5**.
*crystallised from ethanol:toluene.

Three of the alkoxy (**3b**, **3c**, **3d**), and three of the alkylsulfanyl derivatives (**4a**, **4b**, **4d**), crystallised in the triclinic system in space group $P\bar{1}$ (Tables 2 and 3). Among the dialkoxy compounds, the unit cells of **3b** and **3c** have very similar morphology, but those of **3a** and **3d** are very different, the former being monoclinic while the latter has a very different pattern of unit cell edge lengths. Among the dialkylsulfanyl compounds, the unit cells of **4a**, **4b** and **4d** have similar morphologies, with cell length *a* actually decreasing slightly as the alkyl chain length increases, *b* remains about the same, and *c* increases as it is most in alignment with the lengthening alkyl chain direction. In contrast **4c**

crystallises in the monoclinic crystal system. No disorder was modelled in any of the structures and none contained any solvent of crystallisation.

Compound	3a	3b	3c	3d
Formula	$C_{32}H_{38}O_2S_2$	$C_{34}H_{42}O_2S_2$	$C_{36}H_{46}O_2S_2$	$C_{38}H_{50}O_2S_2$
Chain length/Linking atom	7/O	8/O	9/O	10/0
Formula weight	518.74	546.79	574.85	602.90
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.061(2)	7.6682(7)	7.6294(10)	4.4079(2)
b (Å)	9.366(2)	9.3072(8)	9.3554(13)	11.1690(4)
c (Å)	16.661(4)	11.1636(9)	11.4058(16)	17.0294(7)
α (º)	90	102.6670(12)	102.874(2)	94.284(2)
β (º)	100.691(3)	94.2286(13)	93.500(2)	97.301(2)
γ (º)	90	105.6268(13)	103.220(2)	98.842(2)
V (Å³)	1389.4(5)	741.10(11)	767.21(18)	817.90(6)
Z	2	1	1	1
Temperature (K)	150(2)	150(2)	150(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.7749
Calculated density (g.cm^{-3})	1.240	1.225	1.244	1.224
Absorption coefficient (mm^{-1})	0.22	0.21	0.21	0.24
Transmission factors (min./max.)	0.895, 0.943	0.826, 0.988	0.860, 0.954	0.953, 0.986
Crystal size (mm³)	0.52 × 0.27 × 0.27	0.95 × 0.28 × 0.06	0.76 × 0.28 × 0.23	0.20 × 0.07 × 0.06
θ(max) (°)	28.3	30.6	30.6	40.3
Reflections measured	10658	11865	12262	29254
Unique reflections	3455	4498	4659	7930
R_{int}	0.041	0.016	0.020	0.059
Reflections with $F^2 > 2\sigma(F^2)$	2593	3995	4087	6543
Number of parameters	239	254	273	191
R_1 [$F^2 > 2\sigma(F^2)$]	0.043	0.034	0.034	0.050
wR_2 (all data)	0.116	0.094	0.097	0.145
GOOF, S	1.05	1.08	1.05	1.06
Largest difference peak and hole (e Å^{-3})	0.42 and –0.31	0.49 and –0.19	0.49 and –0.19	0.72 and –0.36

Table 2. Crystallographic data for 6,12-dialkoxy-benzo[1,2-*b*:4,5-*b*']*bis*[b]benzothiophenes **3a**-**3d**.

Compound	4a	4b	4c	4d	5
Formula	$C_{32}H_{38}S_4$	$C_{34}H_{42}S_4$	$C_{36}H_{46}S_4$	$C_{38}H_{50}S_4$	$C_{26}H_{25}FOS2$
Chain length/Linking atom	7/S	8/S	9/S	10/S	7/O
Formula weight	550.86	578.91	606.97	635.02	436.58
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	4.9163(4)	4.8575(2)	17.741(11)	4.8430(2)	20.4110(7)
b (Å)	9.6744(7)	9.7907(4)	5.558(3)	9.7919(5)	9.9940(4)
c (Å)	15.8142(12)	16.7849(6)	18.457(11)	18.6253(8)	22.4810(8)
α (º)	104.8989(11)	101.4112(16)	90	81.716(2)	90
β (º)	97.8199(12)	94.3562(17)	118.057(10)	82.641(2)	104.185(2)
γ (º)	95.0448(12)	96.7457(18)	90	83.063(2)	90
V (Å^3)	714.15(9)	773.02(5)	1606.1(16)	862.11(7)	4446.0(3)
Z	1	1	2	1	8
Temperature (K)	150(2)	150(2)	150(2)	150(2)	200(2)
Wavelength (Å)	0.71073	0.7749	0.71073	0.7749	0.7749
Calculated density (g.cm^{-3})	1.281	1.244	1.255	1.223	1.304
Absorption coefficient (mm^{-1})	0.35	0.41	0.32	0.38	0.33
Transmission factors (min./max.)	0.691, 0.983	0.904, 0.988	0.872, 0.994	0.895, 0.996	0.959, 997
Crystal size (mm^3)	1.13 × 0.17 × 0.05	0.25 × 0.07 × 0.03	0.44 × 0.22 × 0.02	0.30 × 0.12 × 0.01	0.13 × 0.05 × 0.01
θ(max) (°)	30.6	40.3	26.4	40.3	32.2
Reflections measured	11394	14583	12037	16243	60518
Unique reflections	4315	7360	3254	8185	12013
R_{int}	0.020	0.024	0.107	0.029	0.040
Reflections with $F^2 > 2\sigma(F^2)$	3816	6299	1992	6239	8684
Number of parameters	239	173	274	191	648
R_1 [$F^2 > 2\sigma(F^2)$]	0.031	0.036	0.058	0.053	0.046
wR_2 (all data)	0.084	0.104	0.145	0.147	0.139
GOOF, S	1.05	1.03	1.03	1.03	1.09
Largest difference peak and hole (e Å^{-3})	0.47 and –0.20	0.60 and –0.53	0.32 and –0.41	0.85 and –0.48	0.31 and –0.35

Table 3. Crystallographic data for 6,12-alkylsulfanyl-benzo[1,2-*b*:4,5-*b*']*bis*[b]benzothiophenes **4a**-**4d** and the monoalkoxy derivative **5**.

Some clear trends in molecular conformation and crystal packing are observable from consideration of the crystal structures. In all cases the alkyl chains were in their fully extended conformations, but the bond angles and dihedral angles around the linking oxygen or sulfur atom varied significantly. The key dihedral angles (Table 4) are 6a-6-X-C1', 6-X-C1'-C2' and X-C1'-C2'-C3' (numbering shown in Scheme 2; X = O or S; C' = alkyl chain carbon), the first of which determines the circular orientation of the alkyl substituent to the plane of the arene core, while the second defines a cone of revolution of the alkyl chain about the linker atom-C1' bond. The third defines the conformation of the extended C-C chain of the alkyl group relative to the heteroatom linker.

The bond angles at the linker atom 6-X-C1' and the adjacent X-C1'-C2' carbon are also listed.

Compound	Chain length/ Linker atom	6a-6-X-C1'	6-X-C1'-C2'	X-C1'-C2'-C3'	6-X-C1'	X-C1'-C2'
		(°)	(°)	(°)	(°)	(°)
3a*	C_7 / O	79.64 (18)	-170.53 (14)	-73.07(19)	112.34 (12)	109.21 (14)
3b	C_8 / O	91.42 (10)	179.48 (8)	66.50 (11)	112.04 (7)	107.86 (7)
3c	C_9 / O	-92.42 (10)	-179.05 (8)	-70.50 (11)	111.47 (7)	108.42 (8)
3d	C_{10} / O	83.59 (10)	-170.54 (7)	60.67 (10)	113.20 (7)	107.84 (7)
4a	C_7 / S	79.26 (8)	70.42 (9)	179.74 (8)	99.88 (5)	113.88 (8)
4b	C_8 / S	-81.65 (7)	-72.38 (7)	-179.64 (7)	99.80 (4)	113.61 (7)
4c*	C_9 / S	110.1 (3)	-75.9 (3)	-178.7 (3)	101.51 (17)	115.1 (3)
4d	C_{10} / S	-98.58 (11)	71.97 (11)	179.50 (10)	99.585 (6)	113.55 (10)

Table 4: Dihedral angles and bond angles at the alkyl substituent–arene linkage (* denotes monoclinic structures).

In the dialkoxy derivatives **3a**-**3d** the angle between the planar arene core and the alkyl substituent at C-6(12) is shallow (Figure 2) in a range from 4.84 – 33.59° (Table 5), with an alkyl chain, a step to the core and another step to the other alkyl chain, with the substituents pointing away from each other as shown for **3a** in Figure 3. The dihedral angles 6a-6-O-C1' defining the circular orientation of the first alkyl chain carbon to the plane of the benzo-bis-benzothiophene core ranged from 79 - 92° while the dihedral angles of the adjacent 6-O-C1'-C2' bonds were 170-179° showing an antiperiplanar arrangement. The oxygen atom lies out of the zig-zag plane of the C-C backbone with the O-C1'-C2'-C3' dihedral angle ranging from 60 – 73° resulting in an approximately gauche conformation. This brings the alkyl backbone plane back to lie approximately parallel to the arene core. The 6-O-C1' bond angles ranged from 111.47 – 113.20° while the adjacent O-C1'-C2' angles were close to tetrahedral ranging from 107.84 – 109.21°.
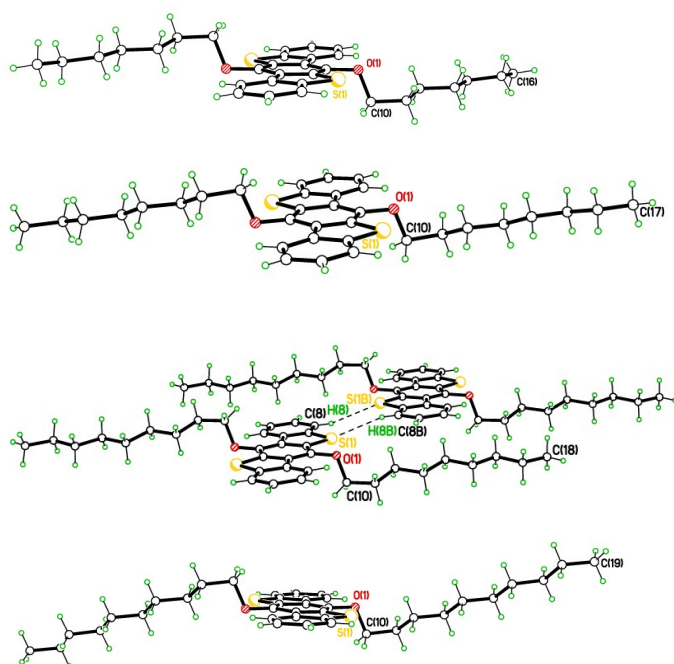
Figure 2: End-on views of X-ray molecular structures of **3a**, **3b**, **3c** and **3d** (C_7-C_{10} chains) showing shallow orientation of oxygen-linked alkyl chains relative to the arene core. Weak head-to-tail C–H•••S interactions are displayed for **3c**.

Compound	Chain length / Linker atom	Angle between arene core and alkyl chain (°)
3a	C7 / O	4.84 (8)
3b	C8 / O	20.43 (3)
3c	C9 / O	15.20 (4)
3d	C10 / O	33.59 (4)
4a	C7 / S	83.226 (18)
4b	C8 / S	82.61 (3)
4c	C9 / S	86.32
4d	C10 / S	81.45 (4)
5*	C7 / O	31.5(2) & 31.3(2)

Table 5: Alkyl chain angle relative to the plane of the benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene core. * Two molecules in the asymmetric unit.
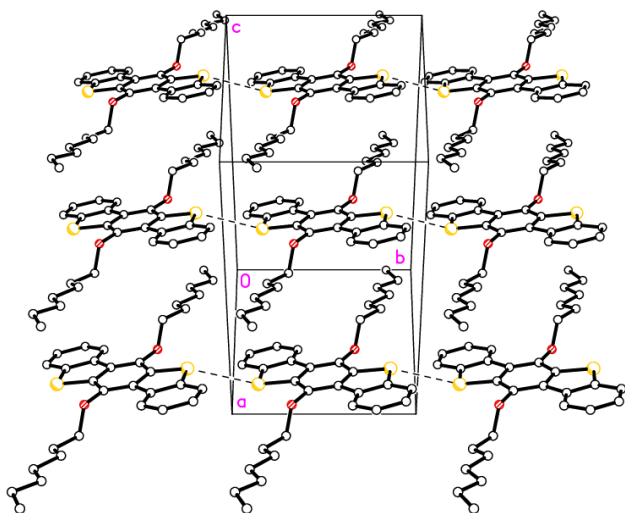
Figure 3: Packing diagram for C_7-O substituted **3a** showing steps from arene core to alkyl chains and gauche conformation about the C1'-C2' bond. S•••S = 3.419 Å.

In contrast, the sulfur-linked alkyl chains are almost perpendicular to the planar aromatic core, subtending angles in the range of 81 – 86°, with the chains also pointing away from each another (Figure 4). The sulfur atoms in **4a**-**4d** lie in the zig-zag plane of the C-C backbone with the S-C1'-C2'-C3' dihedral angles ranging from 178.7 – 179.7° giving an anti-periplanar conformation (Figure 4). The overall orientation of the chain relative to the arene core is thus controlled by the 6a-6-S-C1' dihedral angle which ranges from 79 – 110°. The 6-S-C1' bond angles showed less variation than the corresponding oxygen compounds and were all close, ranging from 99.59 - 99.88° for the triclinic structures and 101.51° for monoclininc **4c**. The adjacent S-C1'-C2' angles were also very similar, ranging from 113.55 – 113.88° for **4a**, **4b** and **4d**, and 115.1° for monoclinic **4c**.
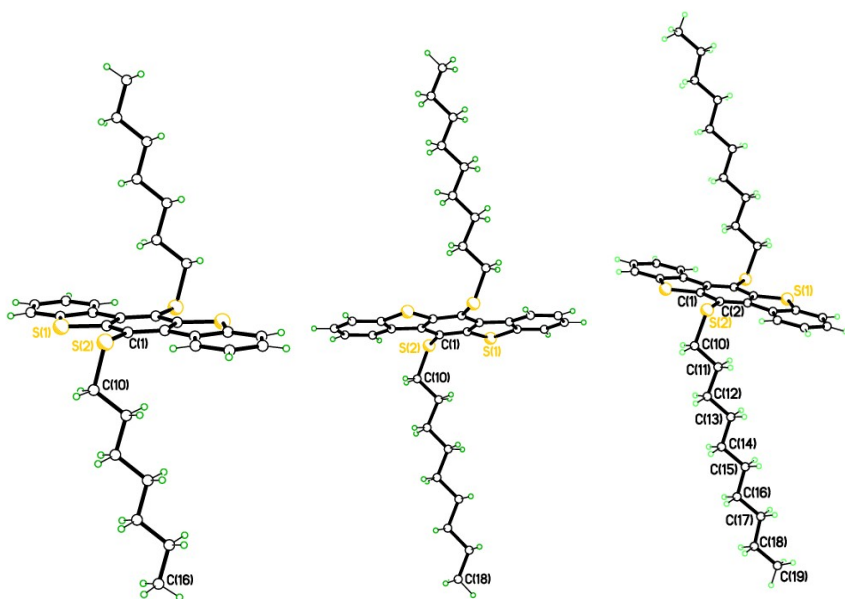
Figure 4: X-ray molecular structures of **4a**, **4b**, **4c**, and **4d** showing conformation of alkyl chains linked through sulfur.

Interdigitation

For both the oxygen- and sulfur-linked compounds, the alkyl substituents interlocked, as illustrated in Figure 5 for decyloxy derivative **3d**, in which seven of the ten alkyl chain atoms interdigitate in the *a*/*b* plane. The fused ring core sections of the molecules form off-set stacks parallel to *a* with closest contacts at *ca*. 3.53Å. No S⋯S interactions were apparent.
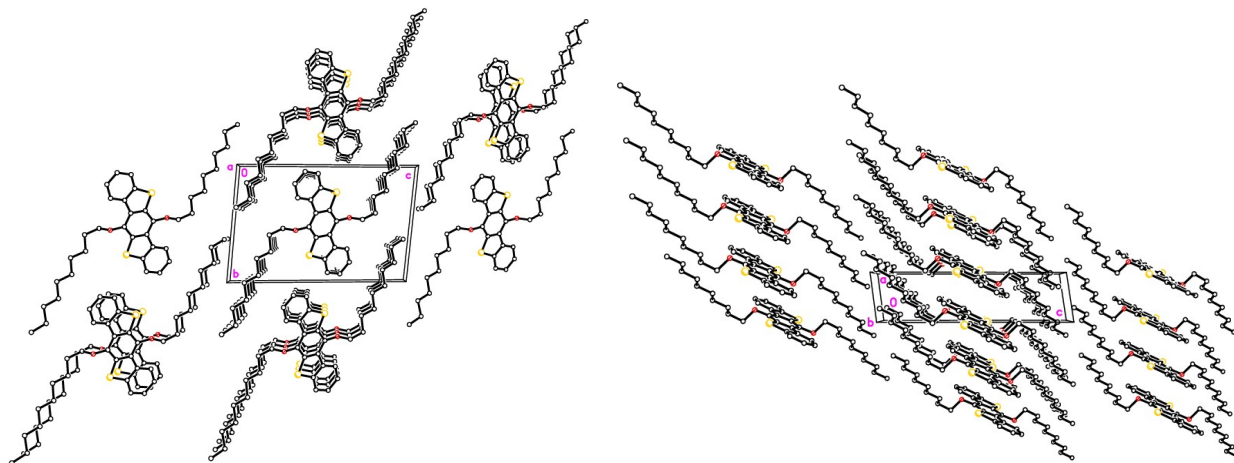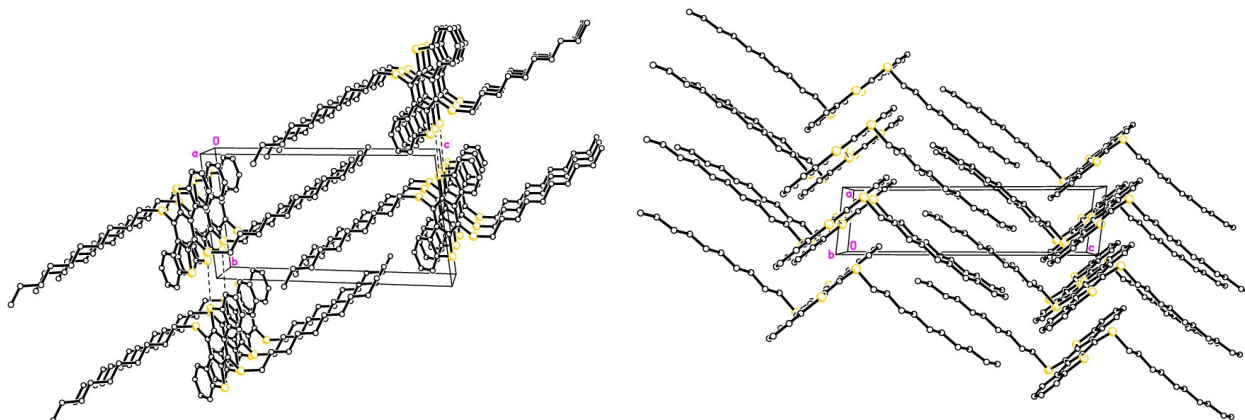

Figure 5: Packing diagram for decyloxy substituted **3d**; views down the *a* (left) and *b* (right) axes showing interdigitation of alkyl substituents.

For the corresponding decylsulfanyl derivative **4d** data was collected at the ALS synchrotron due to the small crystal size. The molecule lies on a centre of symmetry, *i*, and so half is crystallographically unique (Figure 6). The sulfur-bridged decyl chains are almost perpendicular to the planar aromatic core, subtending an angle of 81.45(4)°, with the chains pointing away from one another. Molecules pack with their aromatic cores aligned in columns, which run parallel to the crystallographic *b* axis. The decyl chains bridged to cores within, and between these columns also associate to give columns running parallel to the *b* axis. As for the oxygen analog, the decyl chains have *ca*. seven carbons interlocking, and these separate the columns of cores. The closest contacts between adjacent aromatic cores are *ca*. >4.1 Å, and so π···π stacking is, at best, extremely weak. A single S···S contact is observed between S(1) atoms of molecules in adjacent columns with a separation of 3.643 Å.

Figure 6: Packing diagrams for decylsulfanyl substituted **4d**; views down the *a* (left) and *b* (right) axes showing arene stacks, interdigitation of the decyl chains, and S•••S contacts.

For compound **5**, in which only one substitution had occurred, data was also collected at the ALS synchrotron. The molecular formula was confirmed as $C_{26}H_{25}FOS_2$ and the crystals determined to be monoclininc with no disorder or solvent of crystallisation. There are two molecules in the asymmetric unit. Anisotropic displacement parameters increase gradually along the octyl chains.

Packing.

Molecules π···π stack in groups of four with a centre of symmetry between the two unique molecules. The π-systems are somewhat slipped and do not fully overlap. The octyl chains on neighbouring molecules align approximately parallel (Figure 7). The dihedral angles for the first three bonds of the side chain, namely 12a-12-O-C1', 12-O-C1'-C2', and O-C1'-C2'-C3' are 84.13(17), 164.96(14), and 64.9(2)° respectively, which show the chain adopts a similar orientation to those in the disubstituted aryl ethers **3a-d**. The chain pivots towards the neighbouring thiophene sulfur atom rather than the benzene ring, and the terminal four carbons dip below the plane of the arene core.
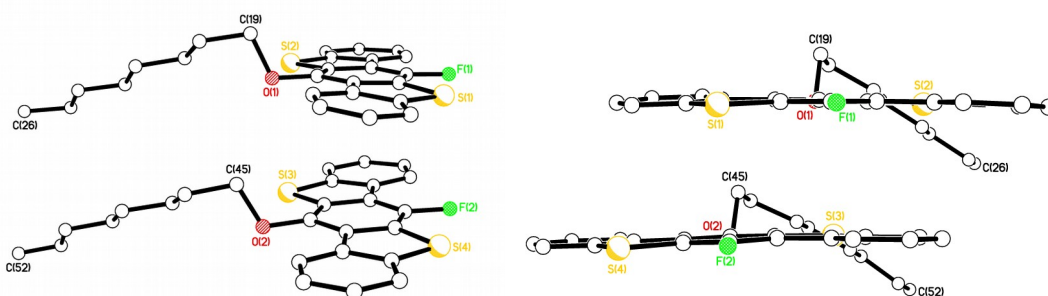
Figure 7: End-on and edge-on views of the mono-substituted 6-fluoro-12-octyloxybenzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene **5** showing the end four carbons of the alkyl chains dropping below the planes of the off-set arene cores.

There is the usual monoclinic herringbone motif between layers (Figure 8). The π···π stacking distances between layers are approximately 3.24 – 3.67 Å for atoms C(27) to C(38) in the second molecule relative to the mean plane of atoms C(1) to C(18) in the first. The two symmetry related π-systems including S(1) and S(2) are separated by 3.40 – 3.60 Å.
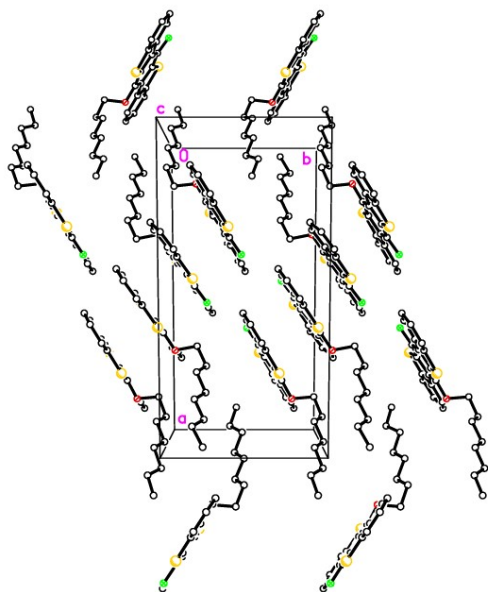
Figure 8: Packing diagram for mono-substituted compound **5**, showing view down the c axis.

COMPARISON WITH RELATED ARYL ALKYL ETHERS AND SULFIDES

A survey of related alkoxy- and alkylsulfanyl-arenes in the CSD was conducted (April 2019) using ConQuest (version 1.21) to compare side-chain orientation in closely related structures. The only reported examples of 6,12-disubstituted benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophenes, contained alkyl groups at the 6,12-positions (CSD codes: DUZGOW,[26] YOJCIK, YOJCOQ, and YOJCUW[28]). Benzo[1,2-*b*:4,5-*b*]dithiophene or anthracene subunits disubstituted with alkoxy or alkylsulfanyl chains with four or more carbons at the central and opposing 4,8- or 9,10-positions respectively, were thus used for the substructure search. Five examples containing a central benzo[1,2-*b*:4,5-*b*]dithiophene core, and carrying two alkoxy groups at the opposing central 4,8-positions were found. In three of these **7** EGOFAJ[29] (C_8-O), **8** XURLON[30] (C_{12}-O), and **9** UCIVOU[31] (C_8-O), the alkoxy chains adopted a similar conformation to compounds **3a-d** with a step from the oxygen to the first methylene group, C1', and a gauche conformation about the C1'-C2' bond (Figure 9).
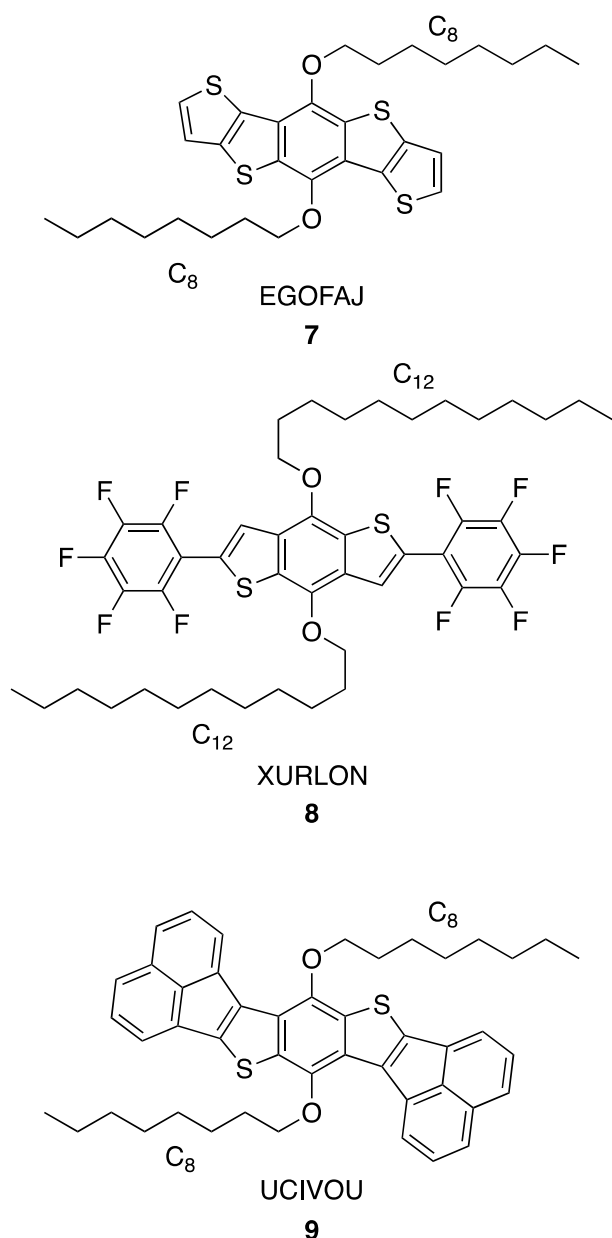
EGOFAJ

7

XURLON

8

UCIVOU

9
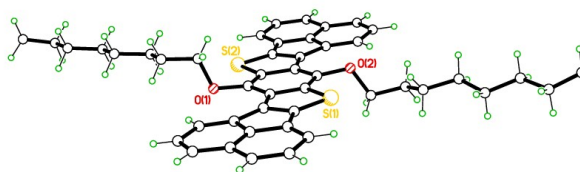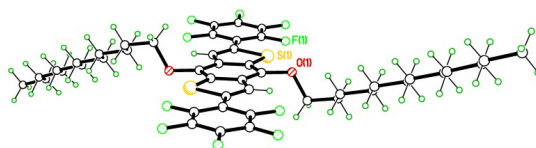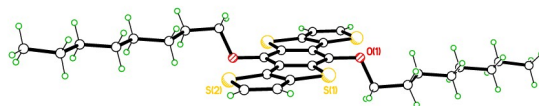
Figure 9: CSD structures displaying similar sidechain conformation to **3a**-**3d** with a step from the core and C3' gauche to oxygen. EGOFAJ and XURLON lie on centres of symmetry, while there are two similar molecules in the asymmetric unit for UCIVOU.

However, two examples **10** EGOKIW[29] and **11** XURLUT[30] (both C_{12}-O) (Figure 10) displayed different side chain arrangements from their close analogues **7** and **8**. The dodecyloxy compound **10** adopted a nearly planar conformation, with the oxygen anti-periplanar to the alkyl chain, and the whole substituent co-planar with the arene core, while **11** displayed a step from the oxygen, but the chains are fully extended with C3' antiperiplanar to the oxygen.
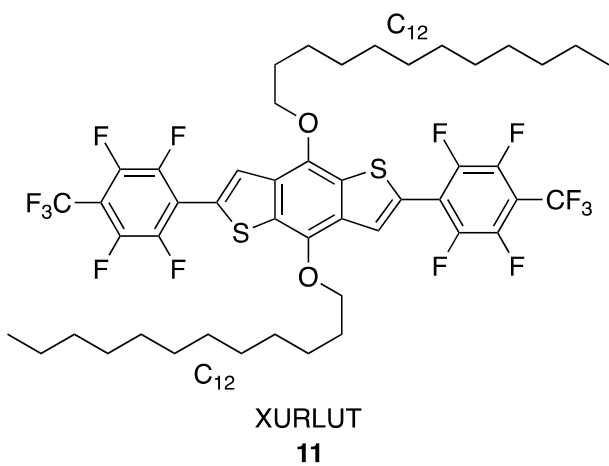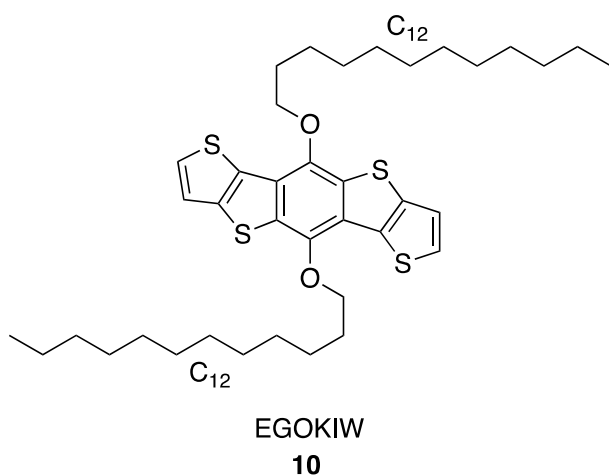
EGOKIW
10

XURLUT
11
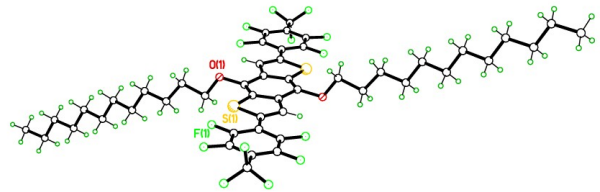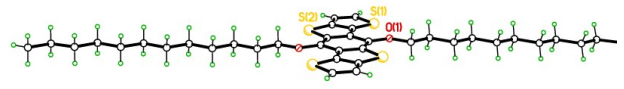
Figure 10: CSD structures with alternative alkoxy substituent conformations. Both lie on centres of symmetry.

Amongst other fused benzenoid compounds bearing alkoxy substituents found from the anthracene substructure search, the step from the core, and a gauche conformation about the C1'-C2' bond found with **3a-d** was quite commonly observed (FAFGEB,[32] UCONOQ[33] and VELTEN[34]) whereas pyrazine-bis-anthracenes (BOPTOR[35] and ZALZAQ[36]) tetra-substituted with octyloxy- or decyloxy groups respectively, also showed a step from the core to oxygen, but the oxygen was anti-periplanar to C3' with the alkyl group sharply angled to the core.

A similar comparison with *para*-disubstituted alkylsulfanyl arenes was made, although fewer examples were found in the database and none based on the central benzo[1,2-*b*:4,5-*b*]dithiophene substructure. Compounds containing *para*-disubstituted benzene fragments were found, and these displayed a range of conformations at the C-S bond (Figure 11). Phthalocyanin JUBPON,[37]

symmetrically substituted at the 1, 4, 8, 11, 15, 18, 22, 25 (all *ortho*-) positions with hexylsulfanyl groups, adopted a nearly completely planar structure. The substituents were fully extended with almost all lying in the plane of the core and turned away from the bridging (6, 13, 20, 27) nitrogen atoms. The groups lead to some twisting of the arene core. A similar conformation was observed for *para*-disubstituted benzene derivative MOBPOK[38] with the hexylsulfanyl groups extended, co-planar and turned away from neighbouring acetylenic substituents. Structure VOCWOB,[39] 1,4-di-*n*-hexylsulfanylphthalonitrile, however adopted a gauche conformation about the C1-C2' bond, but lacked the step from the core to C1' with chains lying in the plane of the arene core. No compounds were found in the database with the arrangement of alkylsulfanyl chains observed for **4a-d**.
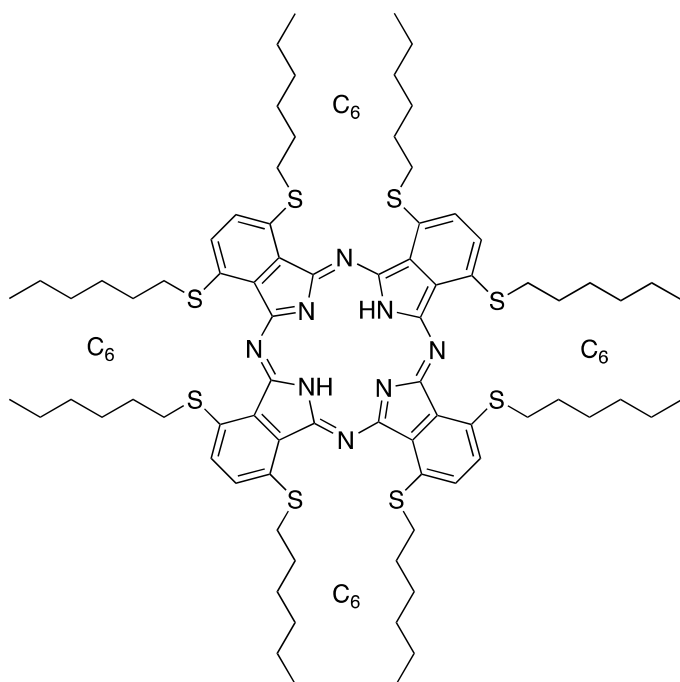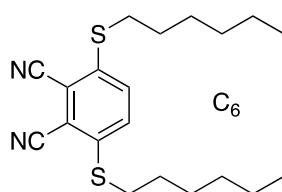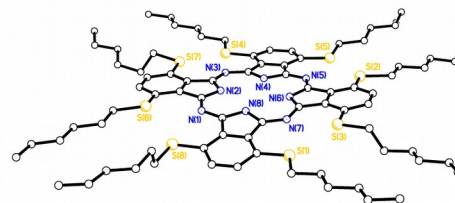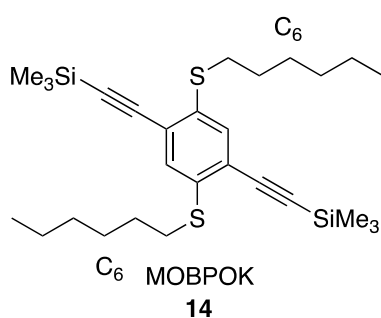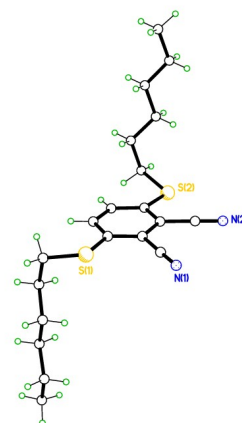
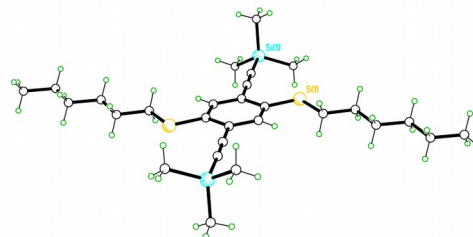Figure 11: *para*-Disubstituted alkylsulfanyl arenes found in the CSD. 12: H atoms omitted for clarity; 13: two similar molecules in the asymmetric unit; 14: lies on a centre of symmetry.

The all hydrocarbon sidechains in the 6,12 dialkyl substituted benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophenes DUZGOW[26] (C$_4$) and YOJCUW[28] (C$_6$) adopted a step to C1' and a gauche conformation about the C1'-C2' bond, similar to the dialkoxy

derivatives **3a**-**3d** described in this work. The hexyl substituents in YOJCIK and YOJCOQ[28] however, adopted a step to C1', and an anti-periplanar conformation for the C1'-C2' bond. The terminal methyl (C6') in YOJCIK[28] was found to be gauche to the rest of the chain, this arrangement not being seen for any other derivatives. In didodec-1-yl substituted benzothieno[3,2-*b*]benzothiophenes the orientation of the alkyl chains varied depending on the ring positions of the substituent (1,6-, 2,7-, 3,8- or 4,9-).[40] In the 2,7-isomer (UBIYIQ) the alkyl chains lie in the plane of the arene core; in the others the chains are angled above and below the plane. Transfer integrals for charge mobility were calculated and shown to be large in the π-stacking direction, and small or zero between layers due to the insulating dodecyl groups. Chain orientation is important to allow close alignment of arene cores and maximum HOMO overlap thus controlling 1D or 2D charge transport.

NMR SPECTROSCOPY

To gain insight into the behaviour of the alkyl substituents on the benzo-bis-benzothiophene core, a solution phase NMR spectrocopic study of compounds **3b** (C_8-O), **4a** (C_7-S), and **4c** (C_9-S), was conducted with examples of three different chain lengths. Both oxygen- and sulfur-linked compounds that formed the distinct and different crystal structures were investigated in solution using ^{1}H and ^{13}C T1 relaxation as a probe for molecular motion. Inversion-recovery (180-delay-90) provided very similar relaxation data for all three compounds tested at both 400 and 500 MHz.

The terminal CH_2-CH_2-CH_3 groups all had ^{1}H and ^{13}C T_1 values (Figure 12) that indicate that they are all very mobile, and these compare well with literature values (^{13}C, 3.1-5.3 s). The inner CH_2 groups showed reduced motion closer to the arene core, as has been observed[41] for decan-1-ol which forms a dimer in solution, such that the OH groups interact and reduce motion at the centre of the dimer. This reduced motion of the CH_2 groups produces T_1 values (^{13}C) of ~0.7-0.9 s.

In both the oxygen and sulfur linked chains the CH_2 T1(^{13}C) values nearest to the O or S, are of the order 0.5-0.9 s and are similar to the literature values. The O-CH_2 values are slightly smaller than for the S-CH_2 which could be due the shorter O-C (~1.425 Å) bond versus S-C (~1.836 Å) that causes slightly

reduced motion (smaller T_1) based on steric considerations. This suggests that the alkyl chains all display a similar motional behaviour and that there is no evidence of the gauche 'kink' in the alkyl chain in the alkoxy derivatives in the solution state.
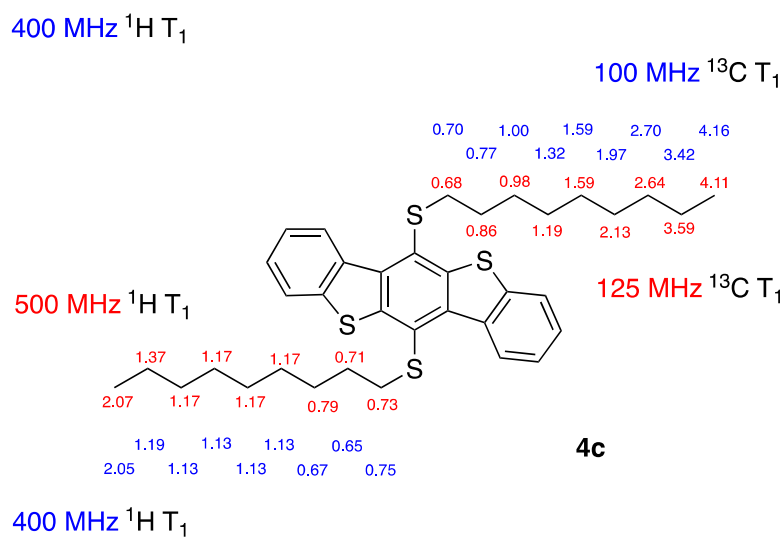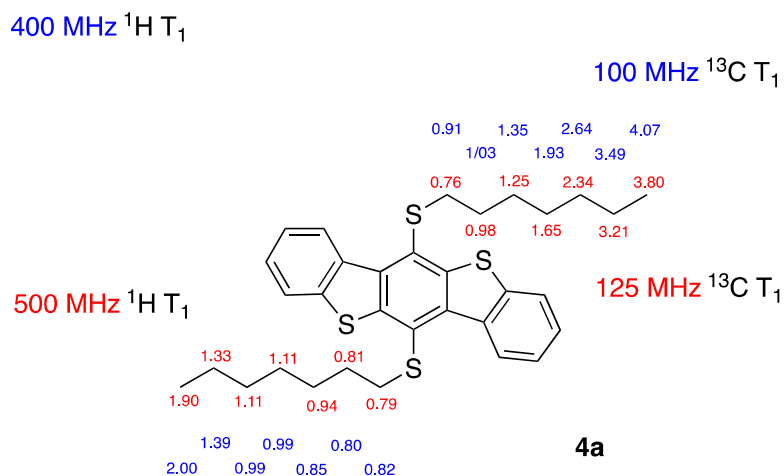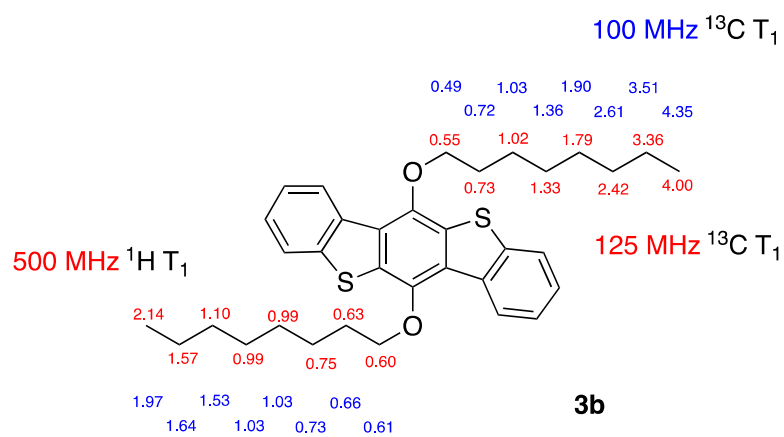
100 MHz ^{13}C T$_1$

0.49   1.03   1.90   3.51
  0.72   1.36   2.61   4.35
0.55   1.02   1.79   3.36
  0.73   1.33   2.42   4.00

500 MHz ^{1}H T$_1$

125 MHz ^{13}C T$_1$

2.14   1.10   0.99   0.63
  1.57   0.99   0.75   0.60
1.97   1.53   1.03   0.66
  1.64   1.03   0.73   0.61

3b

400 MHz ^{1}H T$_1$

100 MHz ^{13}C T$_1$

0.91   1.35   2.64   4.07
  1/03   1.93   3.49
0.76   1.25   2.34   3.80
  0.98   1.65   3.21

500 MHz ^{1}H T$_1$

125 MHz ^{13}C T$_1$

1.33   1.11   0.81
1.90   1.11   0.94   0.79
  1.39   0.99   0.80
2.00   0.99   0.85   0.82

4a

400 MHz ^{1}H T$_1$

100 MHz ^{13}C T$_1$

0.70   1.00   1.59   2.70   4.16
  0.77   1.32   1.97   3.42
0.68   0.98   1.59   2.64   4.11
  0.86   1.19   2.13   3.59

500 MHz ^{1}H T$_1$

125 MHz ^{13}C T$_1$

1.37   1.17   1.17   0.71
2.07   1.17   1.17   0.79   0.73
  1.19   1.13   1.13   0.65
2.05   1.13   1.13   0.67   0.75

4c

400 MHz ^{1}H T$_1$

Figure 12: ^{1}H and ^{13}C T$_1$ values for the alkyl substituents in compounds **3b** (C$_8$-O), **4a** (C$_7$-S) and **4c** (C$_9$-S) indicating free rotation in solution.

CONCLUSIONS

We have synthesised eight benzo[1,2-*b*:4,5-*b'*]*bis*[b]benzothiophenes substituted at the 6,12-positions with alkoxy or alkylsulfanyl groups with chain lengths C$_7$-C$_{10}$, and determined their crystal structures by X-ray diffraction

analysis. One compound with a single octyloxy- substituent at the 6-position was also prepared. The orientation of the substituents was found to vary between oxygen- or sulfur-linked side chains. Alkoxy substituents adopted an arrangement with a step from the arene core to the alkyl chain, and a gauche conformation about the C1'-C2' bond resulting in a shallow angle of the side chain relative to the core. This conformation was found quite commonly in other alkoxy arenes found in the CSD. The alkylsulfanyl chains in sulfur-linked compounds adopted a very different arrangement with a step form the core to the alkyl chain, but with the chain fully extended in an all anti-periplanar conformation, leading to the substituent steeply angled away from the arene core. Alkylsulfanyl arenes in the CSD displayed a wider range of orientations relative to the core, but no examples with the arrangement identified in this work were found. NMR spectroscopic studies suggest the alkyl chains are freely rotating in solution, so the different arrangements adopted in the solid state must be determined by intermolecular interactions during nucleation and crystallisation. Side chain orientation can be important in determining the performance of organoelectronic materials by influencing the alignment of conducting arene subunits, and substituent conformation in the solid state should be considered during the design of new devices. Studies on the electronic and optical properties of compounds **3** and **4** is in progress.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and NMR spectra for compounds **3a**-**d**, **4a**-**d** and **5** and X-ray crystallographic diagrams including displacement ellipsoid plots at the 50% probability level.

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