

Crystal engineering with *p*-substituted 4-ethynylbenzenes using the C–H···O supramolecular synthon

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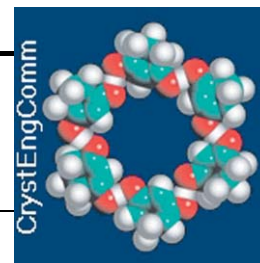
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Paper

The crystal structures of several *para*-substituted ethynylbenzene derivatives; namely, 4-ethynylanisole (**1**), 4-ethynylmethylbenzoate (**2**), 4-ethynylbenzaldehyde (**3**), 4-ethynyl-2,3,5,6-tetrafluoroanisole (**4**), 4-ethynylthioanisole (**5**), and 4-ethynyltoluene (**6**) have been solved from X-ray diffraction data. In **1–4**, the molecular packing consists of infinite chains of molecules, linked by intermolecular $\equiv\text{C–H}\cdots\text{O}$ hydrogen bonds. The structure of **5** contains weak bifurcated $\equiv\text{C–H}\cdots\text{S}$ and $\equiv\text{C–H}\cdots\pi$ ($\text{C}=\text{C}$) interactions and that of **6**, $\equiv\text{C–H}\cdots\pi$ (benzene) interactions.

Introduction

In recent years, there has been much interest in weak hydrogen bonds formed by hydrogen atoms covalently bonded to carbon atoms.¹ The hydrogen atom in a terminal alkyne group has relatively high acidity and forms stronger $\text{C–H}\cdots\text{X}$ hydrogen bonds than most hydrocarbon donors, with either an electronegative atom (e.g., O or N) or the π electron concentration of the triple $\text{C}=\text{C}$ bond acting as the acceptor.²

The crystallography of terminal alkynes is becoming the focus of increasing study, with particular regard towards their applicability for crystal engineering.³ The $\text{C}=\text{C–H}\cdots\text{O}_2\text{N}$ and $\text{C}=\text{C–H}\cdots\text{NC}$ hydrogen bond motifs have been defined as supramolecular synthons by Desiraju.⁴ The former is the dominant motif in the structures of *p*-ethynylnitrobenzene and the 1:1 complex of 1,4-dinitrobenzene and 1,4-diethynylbenzene.⁵ The $\text{C}=\text{C–H}\cdots\text{N}$ motif has been shown to dictate the non-centrosymmetric packing of 4-(4'-ethynylphenylethynyl)-pyridine, which exhibits second harmonic generation (SHG) at 1907 nm exceeding that of urea by a factor of 8.⁶ A similar type of packing with close $\text{C}=\text{C–H}\cdots\text{NC}$ contacts is envisaged in the structure of 4-(4'-ethynylphenylethynyl)-benzonitrile, which shows SHG 16 times larger than that of urea.

Less use has been made of the $\text{C}=\text{C–H}\cdots\text{O}$ motifs in crystal engineering, although it has been shown that close intermolecular $\text{C}=\text{C–H}\cdots\text{O}$ contacts shorter than the sum of the van der Waals radii of H and O (2.68 Å)⁷ occur in many structures.⁸ Herein, we report the crystal structures of 4-ethynylanisole **1**, 4-ethynylmethylbenzoate **2**, 4-ethynylbenzaldehyde **3**, and 4-ethynyl-2,3,5,6-tetrafluoroanisole **4**, determined by single-crystal X-ray diffraction at low temperature, which were expected to contain close $\text{C–H}\cdots\text{O}$ contacts. We also report the structures of 4-ethynylthioanisole **5** and 4-ethynyltoluene **6** for comparison.

Experimental

1 Synthesis

Compounds **1**, **2**, **3** and **5** were prepared by the base-induced hydrosilylation of 4-(trimethylsilylethynyl)anisole,^{9a}

4-(trimethylsilylethynyl)methylbenzoate,^{9b} and 4-(trimethylsilylethynyl)benzaldehyde^{9b} and 4-(trimethylsilylethynyl)thioanisole, respectively, using catalytic amounts of KOH in methanol according to the literature procedures. Compound **4** was formed from the hydrosilylation of (trimethylsilylethynyl)pentafluorobenzene and its subsequent *para*-nucleophilic aromatic substitution by methoxide, which occurs when catalytic amounts of KOH are used in methanol over a period of 10 h. It has been prepared previously by a similar approach using potassium carbonate in DMF.¹⁰ Compound **6** is commercially available.

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Diethylamine was distilled from CaH_2 under N_2 . All other solvents were used as GPR grade. NMR experiments were performed on a Bruker AC200 spectrometer at the following frequencies. ^1H - 200 MHz, ^{13}C - 50.4 MHz, ^{19}F - 188 MHz, and on a Bruker Avance at 100 MHz for ^{13}C . All spectra were recorded in CDCl_3 . ^1H shifts were registered to the internal TMS standard. ^{19}F shifts were registered to the external CFCl_3 standard. FT-IR spectra were recorded as Nujol mulls on Bomem Michelson MB and Perkin Elmer 983 spectrophotometers. GC-MS was carried out using a Hewlett-Packard HP-5890 Series II gas chromatograph equipped with a HP-5971A mass selective detector. A 12 m fused silica (5% cross-linked phenylmethylsilicone) capillary column was used with UHP helium as the carrier gas.

Synthesis of 4-ethynyl-2,3,5,6-tetrafluoroanisole¹⁰ 4. Solid KOH (30 mg, 0.05 mmol) was added to a solution of (trimethylsilylethynyl)-pentafluorobenzene (4.0 g, 15 mmol) in 50 ml of methanol. The reaction mixture was allowed to stir at room temperature for 10 h, and was then extracted with 100 ml diethyl ether. The ether solution was washed three times with 100 ml of 0.2 M HCl solution and three times with 100 ml of water, and dried over Na_2SO_4 . The solvent was removed, and the product was re-crystallised from hexane. Yield: 2.5 g (81%). Mp 56–57 °C (lit.¹⁰ 58–59 °C). ^1H NMR (200 MHz): δ 3.52 (s, 1H), 4.09 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.4 MHz): δ 62.2 (t, J = 4.2 Hz), 68.6 (t, J = 3.7 Hz), 88.5 (m), 96.6 (t, J = 8.0 Hz), 139.7 (m), 140.7 (dm, $^1J_{\text{CF}}$ = 262 Hz), 148.2 (dm, $^1J_{\text{CF}}$ = 257 Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (188 MHz): δ –158.01 (m,

Table 1 Crystal data and refinement parameters

Compound	1	2	3	4	5	6
Formula	C ₉ H ₈ O	C ₁₀ H ₈ O ₂	C ₉ H ₆ O	C ₉ H ₄ F ₄ O	C ₉ H ₈ S	C ₉ H ₈
Formula weight	132.15	160.16	130.14	204.12	148.21	116.15
<i>T</i> /K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	<i>Pbca</i> (# 61)	<i>Pbca</i> (# 61)	<i>P2₁2₁2₁</i> (# 19)	<i>P1</i> (# 1)	<i>P2₁2₁2₁</i> (# 19)	<i>P2₁/c</i> (# 14)
<i>a</i> /Å	14.027(5)	13.962(3)	7.051(1)	4.0302(6)	5.646(1)	5.9008(5)
<i>b</i> /Å	6.124(2)	6.052(1)	8.920(1)	6.240(1)	7.268(1)	10.065(1)
<i>c</i> /Å	17.047(6)	19.542(5)	10.799(1)	8.220(1)	19.528(4)	11.658(1)
α /°	90	90	90	104.97(1)	90	90
β /°	90	90	90	92.28(3)	90	102.919(3)
γ /°	90	90	90	91.73(1)	90	90
<i>V</i> /Å ³	1464.4(9)	1651.3(6)	679.15(1)	199.37(5)	801.4(3)	674.86(9)
<i>Z</i>	8	8	4	1	4	4
ρ_{calc} /g cm ⁻³	1.199	1.289	1.273	1.700	1.228	1.143
μ /mm ⁻¹	0.077	0.090	0.082	0.173	0.320	0.064
2θ max/°	58	58	61	55	56	58
Total reflections	10272	18903	8531	1438	6423	5254
Unique reflections	1923	2220	1215	897	1940	1770
Refls. <i>I</i> > 2 σ (<i>I</i>)	1705	1817	1129	835	1032	1187
Parameters	123	141	116	133	107	114
<i>R</i> _{int}	0.030	0.043	0.036	0.034	0.107	0.054
<i>R</i> [<i>F</i> , <i>I</i> > 2 σ (<i>I</i>)]	0.037	0.043	0.041	0.034	0.050	0.046
<i>wR</i> (<i>F</i> ² , all data)	0.105	0.123	0.116	0.111	0.100	0.088

2F), −137.89 (m, 2F). IR (Nujol, cm^{−1}) $\nu_{\text{C}=\text{C}}$ 2128. MS (EI), *m/z* (rel): 204 (m⁺, 100), 189 (52), 173 (3), 161 (89), 155 (2), 141 (10), 123 (18), 117 (3), 92 (10).

Synthesis of 4-(trimethylsilylethynyl)thioanisole¹¹. 4-Bromothioanisole (5.5 g, 27 mmol), Pd(PPh₃)₂Cl₂ (0.35 g, 0.5 mmol) and CuI (0.05 g, 0.25 mmol) were added to 50 ml of diethylamine under N₂, and trimethylsilylacetylene (4.5 ml, 32 mmol) was added. The reaction mixture was stirred at 55 °C for 8 h. The solvent was removed *in vacuo* and the residue extracted into 200 ml of benzene, and purified by

chromatography on neutral alumina using benzene/hexane (2/3 v/v) as the eluent. Pure 4-(trimethylsilylethynyl)thioanisole was obtained as an oil by microscale vacuum distillation. Yield 5.0 g (91%). ¹H NMR (200 MHz): δ 7.36 (m, 2H), 7.11 (m, 2H), 2.44 (s, 3H), 0.23 (s, 9H). ¹³C{¹H} NMR (50.4 MHz): δ 139.6, 132.2, 125.7, 119.4, 104.9, 94.1, 15.2, 0.1. IR (Nujol, cm^{−1}) $\nu_{\text{C}=\text{C}}$ 2156. MS (EI), *m/z*: 220 (m⁺), 205, 190, 175.

Synthesis of 4-ethynylthioanisole¹² 5. (Trimethylsilylethynyl)thioanisole (4.9 g, 22 mmol) was treated with 0.1 eq. of anhydrous K₂CO₃ in 40 ml of methanol at room temperature

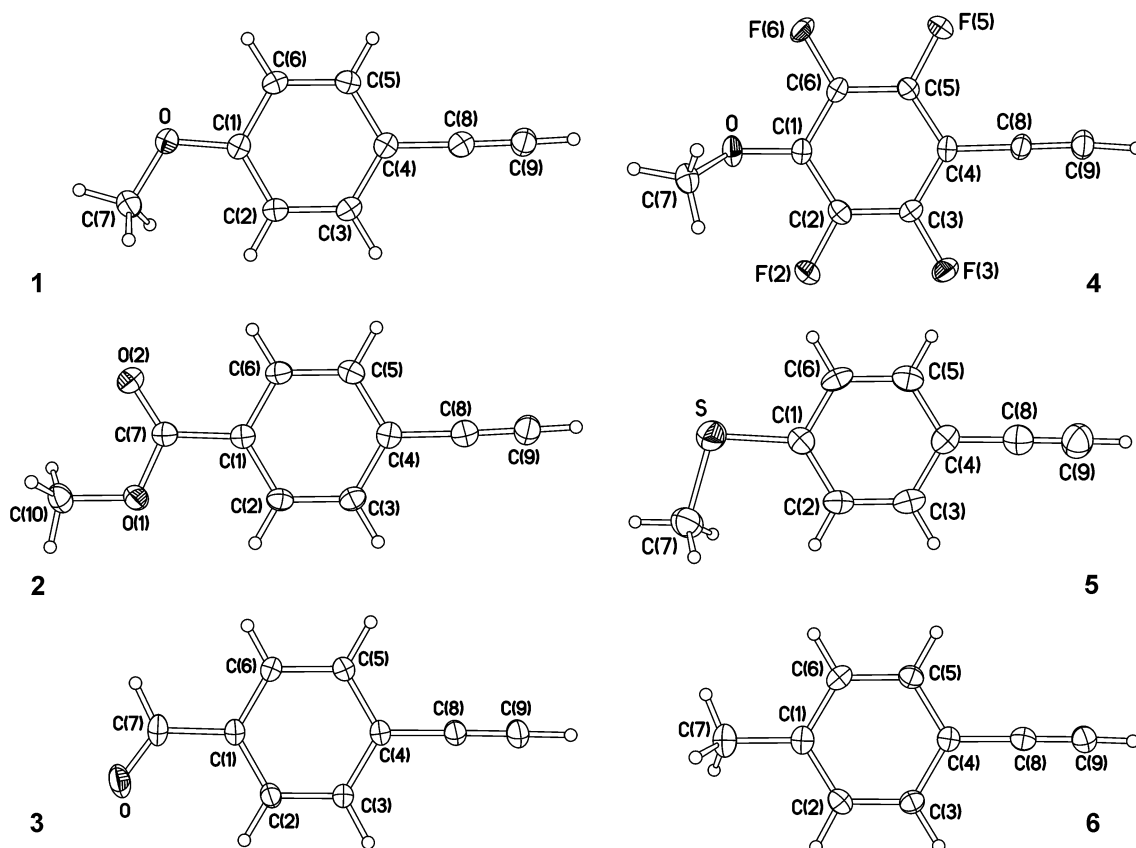
**Fig. 1** Molecular structures of 1–6. Atomic displacement ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond distances (Å), bond and torsion angles (°) in **1–6**

Compound	1	2	3	4	5	6
C(4)–C(8)	1.437(2)	1.438(2)	1.436(2)	1.437(5)	1.433(5)	1.440(2)
C(8)–C(9)	1.199(1)	1.189(2)	1.198(2)	1.190(5)	1.163(5)	1.185(2)
X–C(1)	1.378(1)			1.361(5)	1.763(3)	1.504(2)
X–C(7)	1.435(1)		1.214(2)	1.451(4)	1.797(3)	
C(1)–X–C(7)	117.60(7)			115.4(3)	103.2(2)	
X–C(1)–C(2)	124.33(8)			122.4(4)	124.4(3)	
X–C(1)–C(6)	115.28(8)			119.9(3)	117.0(3)	
C(7)–C(1)–C(2)		122.3(1)	121.1(1)			
C(7)–C(1)–C(6)		117.8(1)	118.7(1)			
C(7)–X–C(1)–C(2)	6.3(1)			68.8(5)	6.2(3)	
O(1)–C(7)–C(1)–C(3)		3.2(1)	3.5(1)			

^a X = O in **1** and **4**, S in **5**, and C(7) in **6**.

for 4 h. After removal of the solvent, the product was extracted with ether and filtered. The pale-yellow liquid was eluted through a short alumina column with benzene/hexane (1:1 v/v) as the eluent. Residual benzene was removed *in vacuo*, and the product solidified at ca. 5 °C. Yield: 3.0 g, (92%). Mp 17–18 °C. ¹H NMR (200 MHz): δ 7.39 (m, 2H), 7.17 (m, 2H), 3.09 (s, 1H), 2.49 (s, 3H). ¹³C{¹H} NMR (100 MHz): δ 140.1, 132.4, 125.8, 118.3, 83.5, 76.8, 15.3. IR (Nujol, cm^{−1}) ν_{C=C} 2108. MS (EI), *m/z*: 148 (m⁺), 133, 115, 102, 89. Anal. Calcd. for C₉H₈S: C 72.93, H 5.44. Found: C 72.73, H 5.42.

2 Crystal structure determinations

Single crystals of **1** formed from a crude, undistilled sample at ca. 5 °C. (Note: terminal alkynes should never be distilled with heating as explosions have been reported).¹³ Single crystals of **2**, **3** and **4** suitable for X-ray diffraction formed by sublimation at ambient temperature and pressure. Single crystals of **5** were prepared *via* sublimation *in vacuo* at 10 °C. Single crystals of **6** were prepared *via* sublimation at ambient pressure at ca. 10 °C over an extended period of time. X-ray diffraction experiments

were performed on Bruker 3-circle diffractometers with SMART 1000 (for **1**, **2**, **4**), SMART 6000 (for **5**) and APEX/ProteumM (for **3**, **6**) CCD area detectors, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from a sealed tube or (for **3**) a 60 W Mo-target microfocus Bede Microsource[®] X-ray generator with glass polycapillary X-ray optics. The low temperature of the crystals was maintained with Cryostream (Oxford Cryosystems) open-flow N₂ cryostats. The low-melting crystals of **5** and **6** were prepared on a slide cooled with dry ice and then transferred directly under the cold N₂ jet. All structures were solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software.¹⁴ All non-H atoms were refined with anisotropic ADP. All H atoms were located by difference Fourier and refined in isotropic approximation except those on the benzene ring in **5** which were treated using a 'riding' model. Crystal data and experimental details are given in Table 1. Full structural data have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference numbers 234595–234600. See <http://www.rsc.org/suppdata/ce/b4/b404502e/> for crystallographic data in CIF or other electronic formats.

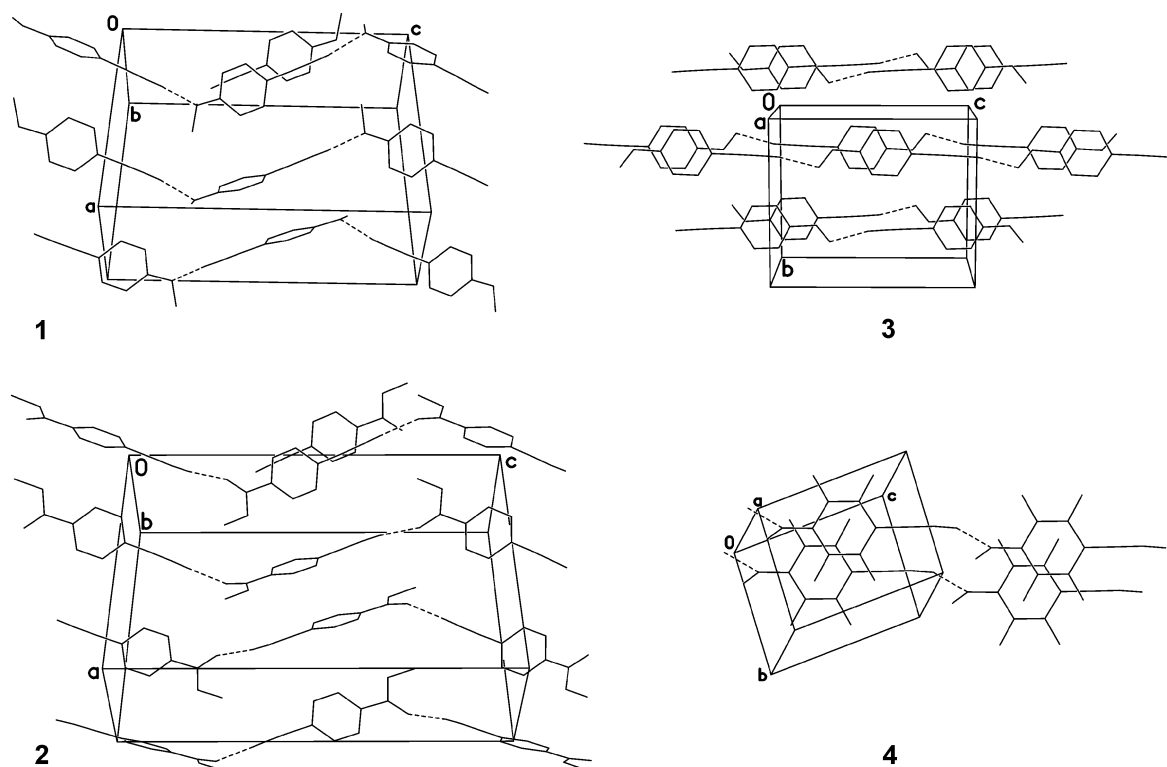


Fig. 2 The crystal packing of **1–4** showing the C–H...O hydrogen bonds. H atoms, other than acetylenic ones, are omitted. Click here to access a 3D image for compound **1**. Click here to access a 3D image for compound **2**. Click here to access a 3D image for compound **3**. Click here to access a 3D image for compound **4**.

Table 3 Hydrogen bonds

	D–H···A	D···A	D–H	H···A	D–H···A
1	C(9)–H···O ($x, \frac{1}{2} - y, z - \frac{1}{2}$)	3.218(2)	0.96(2)	2.26(2), 2.14 ^a	173(1)
2	C(9)–H···O(2) ($x, \frac{1}{2} - y, z - \frac{1}{2}$)	3.111(2)	0.94(2)	2.18(2), 2.04	173(2)
3	C(9)–H···O ($x, y, z - 1$)	3.224(2)	1.02(2)	2.22(2), 2.16	169(2)
4	C(9)–H···O ($x + 1, y + 1, z + 1$)	3.184(4)	1.03(7)	2.35(7), 2.31	138(5)
5	C(9)–H···S ($\frac{1}{2} - x, -y, z - \frac{1}{2}$)	3.673(5)	0.95(4)	3.07(4), 3.00	123(3)
	C(9)–H··· π^b ($\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$)	3.722(7)	0.95(4)	2.93(5), 2.83	140(4)
6	C(9)–H···bz ^c ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$)	3.422(2)	0.96(2)	2.51(2), 2.39	160(1)
	C(9)–H···m ^c ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$)	3.655(2)	0.96(2)	2.71(2), 2.58	172(1)

^a The italicised numbers are calculated assuming an idealised C–H bond length of 1.08 Å (ref. 15). ^b π – midpoint of the C(8)=C(9) bond. ^c bz – centroid of the benzene ring, m – midpoint of the C(5)–C(6) bond of the latter.

Results and discussion

Compounds **1–6** crystallise with one molecule in the asymmetric unit; the molecular structures are shown in Fig. 1 and selected bond lengths, bond and torsion angles are given in Table 2. Each molecule has only one conformational degree of freedom, the twist around the C(1)–O, C(1)–S or C(1)–C(7) bond. In **1**, **2**, **3** and **5** the twist is small, and the resulting steric strain causes these bonds to tilt from the ideal direction, with the O–C–C, S–C–C or C(7)–C–C angles deviating from 120° by up to 9° (as in **1**). Fluorination does not cause any significant change of bond distance in **4** compared with **1**, but effects an out of plane orientation of the methoxy group and consequently a much smaller asymmetry of the O–C(1)–C(2) and O–C(1)–C(6) angles than in **1**. The atomic displacement parameters in **5** exceed those observed in other compounds (at the same temperature) by ca. 50%, indicating a less perfect crystallinity of this low-melting compound.

The crystal packing diagrams for **1**, **2**, **3** and **4** are shown in Fig. 2. The dominant intermolecular interactions in all of them are the C≡C–H···O hydrogen bonds (Table 3) which link the molecules into infinite chains. The crystal packing patterns of **1** and **2** are very similar, centrosymmetric (space group *Pbca*). In contrast, compounds **3** and **4** crystallise in the chiral space groups *P2₁2₁2₁* and *P1*, respectively. In each structure there is one molecule per asymmetric unit. Molecules linked by hydrogen bonds in structures **1** and **2** are related by a *c* glide plane, and their benzene rings form dihedral angles of 57.5° and 51.2°, respectively.

In structure **3**, such molecules are related by the *c* translation, and in structure **4**, by an *a* + *b* + *c* translation; hence, in both structures, the planes of all molecules within a chain are parallel. Thus, the presence of fluorine atoms in **4** completely alters the mode of crystal packing compared with **1**. It is noteworthy that the crystal of **4** is polar and therefore deserves checking for potential SHG activity. The hydrogen bonds in **1–3** are very short and nearly linear; that in **4** is considerably longer and strongly non-linear, probably due to the existence of an additional close contact C≡C–H···F(5) (H···F 2.55 Å, cf. the sum of van der Waals radii 2.56 Å⁷). The fluorine atom is known as a poor acceptor of hydrogen bonds;¹⁶ nevertheless it can compete with a C≡C bond for being an acceptor of a C–H···X bond. Thus, the crystal structures of most *p*-halogenoethynylbenzenes display C≡C–H··· π (C≡C) interactions, except that of *p*-fluoroethynylbenzene, which contains C≡C–H···F contacts of 2.26 Å, the closest observed so far.¹⁷ In the structures of some fluorinated 1,4-diethynylbenzenes, the presence of fluorine atoms can significantly change the crystal packing, even if they themselves do not participate in hydrogen bonds.¹⁸

The crystal packing of **5** and **6** is shown in Fig. 3. The acetylenic hydrogen in **5** forms a bifurcated hydrogen bond with the sulfur atom of one adjacent molecule, and the C≡C bond of another molecule. This gives rise to a 3-dimensional network. However, the bonding is rather weak. The H··· π (C≡C) distance is 0.23 Å longer than in the structure of

1,4-diethynylbenzene^{3a} (2.60 Å), and the S···H distance exceeds the sum of van der Waals radii⁷ (2.92 Å). The structure of **6** comprises centrosymmetric pairs of molecules, contacting face-to-face with the interplanar separation of 3.48 Å. These dimeric units form a herring-bone motif, similar to that observed in pyrene and a few other fused-ring aromatic hydrocarbons.¹⁹ Surprisingly, the acetylenic H atom does not form a C≡C–H··· π (C≡C) hydrogen bond, as in 1,4-diethynylbenzene^{3a,b} and 1-halo-4-ethynylbenzenes¹⁷ but instead points toward the benzene ring, between its centre and the C(5)–C(6) bond.

Conclusion

It has been shown that the crystal structures of 4-ethynylanisole, 4-ethynylmethylbenzoate, 4-ethynylbenzaldehyde and 4-ethynyl-2,3,5,6-tetrafluoroanisole are composed of infinite chains of molecules joined by C≡C–H···O hydrogen bonds. The molecular packing of the first three are very similar, with molecules in adjacent chains being oriented in opposite directions. However, the molecules of 4-ethynyl-2,3,5,6-tetrafluoroanisole are all aligned in the same direction, which must be attributed to the fluorine atoms, and should lead to solid state SHG activity. Thus, the C≡C–H···O motif can be considered to be a supramolecular synthon, which is realised in preference to C≡C–H··· π synthons. In contrast, in 4-ethynylthioanisole there is a competition between C≡C–H···S and C≡C–H··· π (C≡C) synthons. The structure of 4-ethynyltoluene is dominated by the C≡C–H··· π (benzene), rather than C≡C–H··· π (C≡C) interactions.

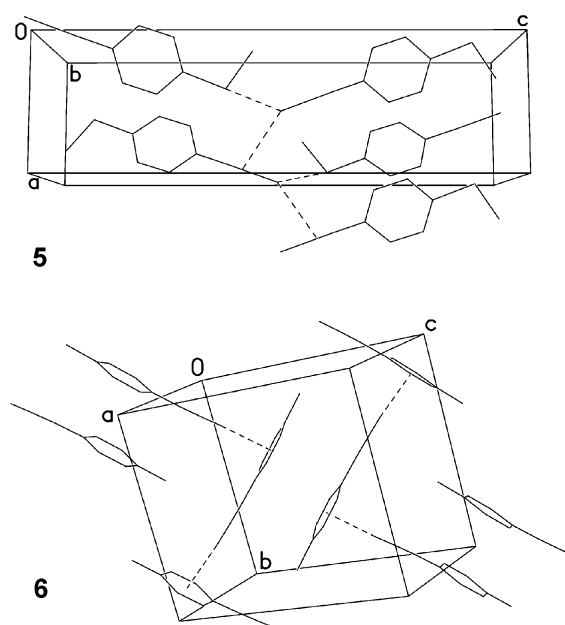


Fig. 3 The crystal packing of **5** and **6**. Click here to access a 3D image for compound **5**. Click here to access a 3D image for compound **6**.

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