

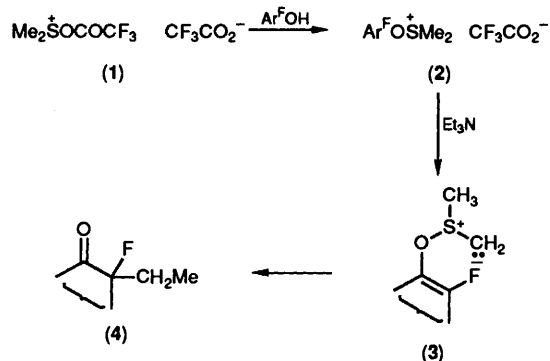
Partially Fluorinated Heterocyclic Compounds. Part 27.¹ The Synthesis of 4,5,6,7-Tetrafluorobenzo[*c*]thiophene and 4,5,6,7,8,9-Hexafluoronaphtho[1,2-*c*]thiophene; some Chemistry and Electrochemistry

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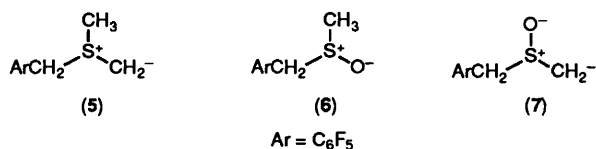
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2,3,4,5,6-Pentafluorobenzyl methyl sulphoxide (**6**) is readily converted by butyl-lithium into 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**8**) and 1,3,4,5,6,7,8-heptafluoro-2-naphthylmethyl methyl sulphoxide (**9**) in a similar manner gives a very low yield of 4,5,6,7,8,9-hexafluoronaphtho[1,2-*c*]thiophene (**11**) accompanied by the 7- and 8-butylated derivatives (**12**) and (**13**) respectively, and also 1,3,4,5,6,7,8-heptafluoronaphthalene-2-carbaldehyde (**10**). Compound (**8**) undergoes Diels–Alder addition reactions followed by sulphur elimination with dimethyl acetylenedicarboxylate and tetrafluorobenzene to give the naphthalene and anthracene derivatives (**14**) and (**15**) respectively. With lithium propane-2-thiolate, compound (**8**) gives the 5-propan-2-ylthio and 5,6-bispropan-2-ylthio derivatives (**16**) and (**17**) respectively. Compound (**8**) is polymerised by $\text{SbF}_5\text{--HF}$ to poly(1,3-dihydro-4,5,6,7-tetrafluorobenzo[*c*]thiophene) (**20**). The electrochemical anodic oxidation of (**8**) has been studied extensively: polymer (**20**) is produced accompanied by a deep red material readily soluble in chloroform, which is not poly(4,5,6,7-tetrafluorobenzo[*c*]thiophene) (**24**).

In a previous paper we reported examples of 2,3-sigmatropic (*i.e.* Sommelet–Hauser) rearrangements in some polyfluoroaromatic and -heteroaromatic systems in which an *ortho* carbon bearing a fluorine, or an *ortho* nitrogen was the migration terminus.² Polyfluoroarenes and -heteroarenes were treated with the complex (1) formed from dimethyl sulphoxide (DMSO) and trifluoroacetic anhydride, followed by treatment of the oxysulphonium salt (2) with triethylamine: the ylide (3) rearranged to give dearomatized materials (4) (Scheme 1). We

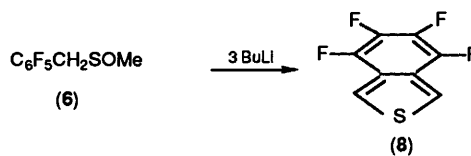


have also shown that the ylide (5) derived from 2,3,4,5,6-pentafluorobenzyl dimethylsulphonium bromide and butyl-lithium gave a complex series of products following an initial 2,3-sigmatropic rearrangement,³ while 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6), which is isomeric with (3) derived from pentafluorophenol, followed a completely different course of reaction on thermolysis.⁴ We considered yet another candi-



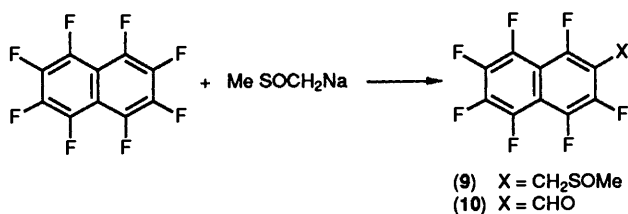
date (7), derived from (6), as potentially capable of undergoing a 2,3-sigmatropic shift in view of its close similarity to (5). Hendrickson had shown that the sulphone $\text{CF}_3\text{SO}_2\text{CH}_2\text{SO}_2\text{Me}$ underwent dilithiation of the CH_2 group with two equivalents of butyl-lithium,⁵ and we report in this paper the reaction of the sulphoxide (6) with 3 equivalents of butyl-lithium which was expected to create the carbanionic functionality SO^-CH_2^- required in (7) for the proposed reaction.

2,3,4,5,6-Pentafluorobenzyl methyl sulphoxide (6)⁴ was treated with the butyl-lithium in tetrahydrofuran at -70°C and the mixture allowed to warm slowly, whereupon a mildly exothermic reaction occurred at -10°C . 4,5,6,7-Tetrafluorobenzo[*c*]thiophene (**8**) (27%) a volatile solid was isolated with ease from the reaction product (Scheme 2), the overall reaction



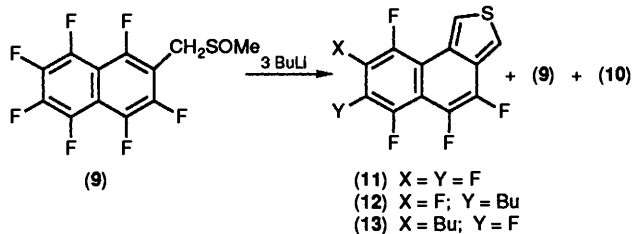
being nucleophilic replacement of *ortho* fluorine by CH_2Li and dehydration. No other products were isolated which would have indicated any initial 2,3-sigmatropic rearrangement. Unlike benzo[*c*]thiophene itself,⁶ compound (8) was relatively stable over short periods of time in air at room temperature, and indefinitely stable at -18°C . The tetrafluorobenzo unit has been shown to exert a similar stabilising effect in tetrafluoroisindole⁷ and tetrafluorobenzo[*c*]furan.⁸

We have explored the cyclisation reaction further using 1,3,4,5,6,7,8-heptafluoro-2-naphthylmethyl methyl sulphoxide (9) prepared in 34% yield according to Scheme 3. A small amount of the aldehyde (10) (7%) was also isolated from the reaction product; under different conditions benzaldehyde has been obtained from benzyl methyl sulphoxide.⁹ The substituents were shown to be at the 2-position in (9) and (10) by the presence of two large *peri* $J_{\text{F--F}}$ coupling constants in the ¹⁹F NMR of each compound. Treatment of the sulphoxide (9) with



Scheme 3.

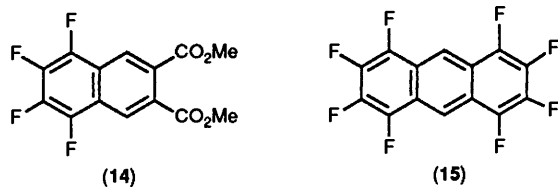
butyl-lithium as before gave 4,5,6,7,8,9-hexafluorobenzene[1,2-*c*]thiophene (11) (5%), an inseparable mixture of the 7- and 8-butyl derivatives (12) and (13) in the ratio of 5:95 respectively (1.5%), the aldehyde (10) (50%), and unchanged (9) (20%) (Scheme 4). The mode of ring fusion of the cyclised products



Scheme 4.

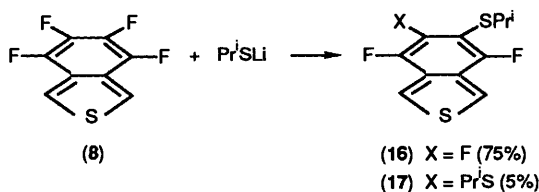
(11), (12), and (13) was deduced as having taken place by substitution of the 1-F in (9), since there was only one large J_{F-F} coupling constant in the ¹⁹F NMR spectrum of each compound, while the site substitution of the butyl groups in (12) and (13) was based on chemical shift considerations.

We have examined the reactions of 4,5,6,7-tetrafluorobenzene[*c*]thiophene (8) towards dienophiles. With dimethyl acetylenedicarboxylate at 130 °C, and with tetrafluorobenzene (generated by allowing pentafluorophenyl-lithium to warm from -78 °C to room temperature),¹⁰ compounds (14) and



(15)¹¹ respectively were formed as a result of the heterocyclic ring of (8) behaving as a diene followed by loss of sulphur from the initial adduct.

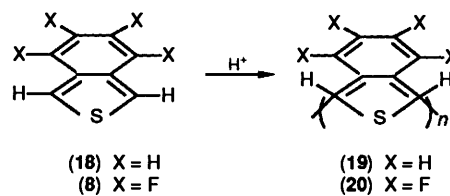
Lithium propane-2-thiolate reacted with the benzo[*c*]thiophene derivative (8) in THF at room temperature over 70 h as shown in Scheme 5. Only the starting material (8) could be



Scheme 5.

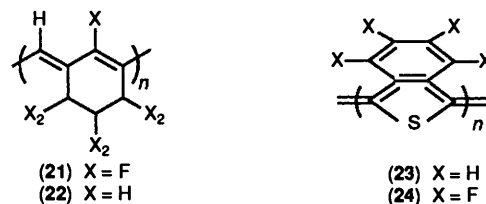
separated for the product, while the structures of (16) and (17) in the remaining mixture were deduced from a consideration of chemical shift data in the ¹⁹F NMR spectrum. The sensitivity of compounds (16) and (17) to the atmosphere prevented their full characterisation.

Benzo[*c*]thiophene (18) readily undergoes polymerisation with methanesulphonic acid to give the poly(1,3-dihydrobenzo[*c*]thiophene) (19).¹² In the same way the tetrafluoro compound (8) was converted into polymer (20) by 'magic acid' (SbF₅-HF) (Scheme 6).



Scheme 6.

Particular interest has been shown in recent years in conjugated polymers as electrically conducting materials, with poly(acetylene), (CH=CH)_n being the material most studied.¹³ In 1979 Fukui proposed that the replacement of half or all of the hydrogen in poly(acetylene) should provide air stable materials in the form of compounds -(CH=CF)_n and -(CF=CF)_n which would have higher intrinsic conductivities and have greater capacities for becoming n-type conductors.¹⁴ Support for some of these conclusions has been found in compound (21) which is oxidatively more stable and has a conductivity *ca.* 10⁷ higher than (22).¹⁵ A number of heterocyclic compounds such as



poly(pyrrole)¹⁶ and poly(thiophene)¹⁷ have been prepared by the electrochemical polymerisation of the parent heterocycle at the anode and have been found to be much more stable to atmospheric exposure than poly(acetylene). Very specific conditions were described in 1984 for conversion of benzo[*c*]thiophene (18) into polybenzo[*c*]thiophene [poly(isothianaphthene)] (23),¹² a material which has attracted special attention because it has a band gap of only 1 eV.* It was of profound interest, therefore, to attempt the analogous conversion of 4,5,6,7-tetrafluorobenzene[*c*]thiophene (8) into the poly(tetrafluorobenzene[*c*]thiophene) (24) since, although not involving C-F bonds directly on the main polymer backbone, the absence of hydrogen should render (24) even less susceptible to atmospheric oxidation than the unsubstituted polymer.

Wudl successfully prepared polymer (23) using a freshly prepared sample of benzo[*c*]thiophene (18) in acetonitrile using Ph₄AsCl or Ph₄PtCl as the supporting electrolyte and a tin oxide coated glass anode.¹² The chloride counter-ion was vital to suppress completely the formation of poly(1,3-dihydrobenzo[*c*]thiophene) (19) which appeared as a copious white precipitate in the anode compartment when Bu₄NBF₄ was the supporting electrolyte. The chloride ion was presumed to be more nucleophilic than (18) and so interrupted the cationic propagation step following electrochemical initiation by 'nascent' p-doped poly(benzo[*c*]thiophene) (and therefore a polymeric cation) which was observed to be formed initially as a blue film.

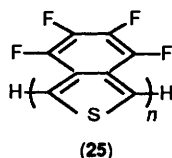
Cyclic voltammetry enabled the conditions to be established

* 1 eV ≈ 1.602 × 10⁻¹⁹ J.

for the anodic oxidation of 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**8**). Using a heavy gold anode, with acetonitrile and Bu_4NBF_4 as the supporting electrolyte, a blue deposit was formed on the anode. However, when the solvent was evaporated in air, the mixture became deep red and was totally soluble in chloroform. Chromatography of the product on silica gel using solvents of increasing polarity (CCl_4 , CHCl_3 , and $\text{CH}_3\text{CO}_2\text{Et}$) gave poly(1,3-dihydro-4,5,6,7-tetrafluorobenzo[*c*]thiophene) (**20**) and a deep red-black lustrous solid, (**Q**) (see later). Similar results were obtained using liquid sulphur dioxide in place of acetonitrile.

Attempts were made to eliminate the formation of (**20**), formed by the electrochemically induced cationic polymerisation of the benzo[*c*]thiophene (**8**) by using Ph_4PCl as the supporting electrolyte: no coloration appeared at the anode, which became badly etched, presumably because of preferential discharge of chlorine which attacked the gold. A number of fluoride ion salts were tried as a source of a non-dischargeable nucleophile, but the main problem was that of solubility. Silver fluoride is soluble in acetonitrile and was examined as the supporting electrolyte in the electrolysis of benzo[*c*]thiophene (**18**) at a gold anode. An irregular blue-black deposit of poly(benzo[*c*]thiophene) (**23**) was formed at the anode, but was accompanied by the formation of the poly-1,3-dihydro compound (**19**). When the experiment was repeated using 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**8**), no coloration at all appeared at the anode. Using Bu_4NF or CsF in conjunction with (**8**)-acetonitrile- Bu_4NBF_4 some blue deposit (**Q**) was formed at the gold anode, but it was also accompanied by poly(1,3-dihydro-4,5,6,7-tetrafluorobenzo[*c*]thiophene) (**20**), showing that the fluoride ion had not been effective in eliminating the cationic polymerisation process with either substrate (**18**) or (**8**).

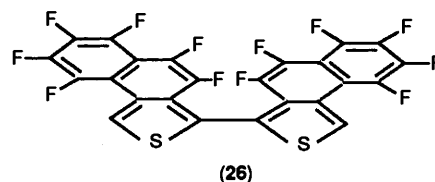
The mass spectrum of the electrochemically produced compound (**Q**) was remarkable in that it showed masses corresponding to oligomeric materials (**25**) ($n = 1, 2, 3$, and 4),



yet the ^1H NMR excluded the possibility of such individual species since there were no signals in the region of 7.9 ppm found in (**8**); there were two broad signals at *ca.* 0.94 and 1.25 ppm. Compound (**Q**) showed two broad singlets at -148.4 and -158.1 ppm [*c.f.* -149.1 and -162.8 ppm in (**8**)]. Gel permeation chromatography of (**Q**) indicated a material containing about 20 heterocyclic units, though in other experiments, material was obtained which appeared to contain as low as 9 and as high as 30 heterocyclic units. Even the material with the smallest molecular weight would not be expected to be soluble in chloroform to the degree which was observed.

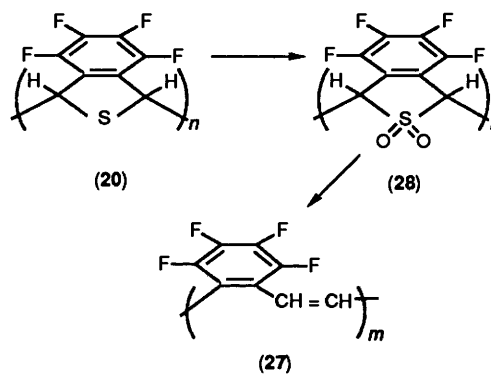
The blue colour of the material deposited on the gold anode was indicative of a cationic (p-doped) species insoluble in acetonitrile which on contact with air became undoped and consequently soluble as the red-black material (**Q**). When (**Q**) was added to concentrated sulphuric acid a blue solution formed, indicative of p-doping. It was not unexpected that a poly(4,5,6,7-tetrafluorobenzo[*c*]thiophene) (**24**) would be unstable towards poly-cation formation (p-doping), and no satisfactory conclusion could be reached from the attempted n-doping experiment in which sodium naphthalenide was added to a solution of (**Q**) in THF.

The inescapable conclusion for all these experiments is that poly-(4,5,6,7-tetrafluorobenzo[*c*]thiophene) (**24**) had not been formed in the electrochemical cell.



The electrochemical oxidation of 4,5,6,7,8,9-hexafluoronaphtho[1,2-*c*]thiophene (**11**) in liquid SO_2 at -20°C using Bu_4NBF_4 as the supporting electrolyte and a gold anode gave an uneven blue-black deposit which turned orange-yellow in air and was completely soluble in chloroform. Mass spectrometry of the crude product indicated the presence of the dimer (**26**), but the reaction was not investigated further.

During the course of this work the possibility of preparing poly(*o*-tetrafluorophenylenevinylene) (**27**) from polymer (**20**) became evident (Scheme 7). Compound (**28**) was formed by



Scheme 7.

treating (**20**) with *m*-chloroperbenzoic acid but on thermal pyrolysis it failed to undergo the chelotropic extrusion of SO_2 and gave a carbonised product.

Experimental

NMR spectra were obtained with a Bruker AC250 instrument [^1H (250 MHz) and ^{19}F (235 MHz)]. Chemical shifts are positive up frequency (downfield) from TMS and CFCl_3 , hence all ^{19}F resonance values are negative]. Mass spectroscopy data were obtained with a VG 7070E instrument. Molecular ions M^+ are quoted for electron ionisation.

Reaction of 2,3,4,5,6-Pentafluorobenzyl Methyl Sulphoxide (6) with Butyl-lithium.—The sulphoxide (**6**) (13.98 g, 57.3 mol) in dry THF (250 ml) was treated at -70°C with butyl-lithium in hexane (1.715 M; 105 ml, 180 mmol) over 30 min and stirred for 3 h. The mixture was warmed whereupon a mildly exothermic reaction occurred at -10°C , and after 1 h at $<0^\circ\text{C}$ the mixture was acidified with sulphuric acid (2 M) and extracted with ether. The extracts were dried (MgSO_4), the solvent evaporated, and the dark oily residue sublimed *in vacuo* at $25^\circ\text{C}/0.005$ mmHg to give the crude product (5.1 g). Recrystallisation from light petroleum (b.p. 40 – 60°C) gave 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**8**) (3.14 g, 27%), m.p. 53.5 – 55.5°C (Found: C, 46.95; H, 0.85; M^+ , 206. $\text{C}_8\text{H}_2\text{F}_4\text{S}$ requires C, 46.6; H, 0.98%; M , 206); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.87 (1-H/3-H); $\delta_{\text{F}}(\text{CDCl}_3)$ -149.1 (4-F/7-F) and -162.8 (5-F/6-F); λ_{max} 3 130 cm^{-1} (CH).

Cyclic voltammetry established the oxidation potential of (**8**) in acetonitrile with Bu_4NBF_4 as the supporting electrolyte at $+1.51$ V relative to the standard calomel electrode.

Reaction of Octafluoronaphthalene with Sodium Methylsulphynylmethanide.—Octafluoronaphthalene (10 g, 36.8 mmol) in dry THF (160 ml) was treated at -70°C with sodium methylsulphynylmethanide in DMSO (2.68M; 27.5 ml, 73.7 mmol) over 1 h and stirred for a further 3 h. Water (60 ml) was added, the mixture was warmed to room temperature, diluted with water, and extracted with ether. Evaporation of the solvents from the dried (MgSO_4) extracts gave a brown oil which on sublimation at $45^{\circ}\text{C}/0.005$ mmHg gave the crude product (4.1 g, 34%) which on recrystallisation from ethanol–light petroleum (b.p. 60 – 80°C) gave 1,3,4,5,6,7,8-heptafluoro-2-naphthylmethyl methyl sulphoxide (**9**) m.p. 113.5 – 114°C (Found: C, 43.45; H, 1.35%; M^+ , 330. $\text{C}_{12}\text{H}_5\text{F}_7\text{OS}$ requires C, 43.64; H, 1.52%; M , 330); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.68 (s, CH_3), 4.23 and 4.32 (AB, J_{AB} 13 Hz; CH_2); $\delta_{\text{F}}(\text{CDCl}_3)$ -118.1 (dd, 1-F), -136.3 (br d, 3-F), 143.3 (dt, 8-F), -145.5 and -147.5 (both dt unassigned 4-F, 5-F), -151.9 and -154.5 (both m, unassigned 6-F, 7-F, $J_{1-\text{F},8-\text{F}}$ 68, $J_{1-\text{F},8-\text{F}}$ 68, $J_{4-\text{F},5-\text{F}}$ 55 Hz). A closer examination of the first sublimate from larger scale reactions revealed the presence not only of octafluoronaphthalene but also 1,3,4,5,6,7,8-heptafluoronaphthalene-2-carbaldehyde (**10**) m.p. 89 – 90°C [from light petroleum (b.p. 40 – 60°C)]. (Found: C, 46.75; H, 0.2%; M^+ , 282. $\text{C}_{11}\text{HF}_7\text{O}$ requires C, 46.81; H, 0.36%; M , 282); $\delta_{\text{H}}(\text{CDCl}_3)$ 10.48 (s, CHO); $\delta_{\text{F}}(\text{CDCl}_3)$ -121.6 (dd, 1-F), -140.8 (dm, 8-F), -143.3 (t, 3-F), -144.8 and -147.9 (unassigned 4-F, 5-F), -147.7 and -153.7 ppm (both m, unassigned 6-F, 7-F); $J_{1-\text{F},8-\text{F}}$ 72.5, $J_{4-\text{F},5-\text{F}}$ 58 Hz.

Reaction of 1,3,4,5,6,7,8-Heptafluoro-2-naphthylmethyl Methyl Sulphoxide (9) with Butyl-lithium.—The sulphoxide (**9**) (2.49 g, 7.55 mmol) in dry THF (250 ml) was treated at -70°C with butyl-lithium in hexane (1.48 M; 15.3 ml, 22.6 mmol) over 30 min, stirred for a further 4 h and worked up as for (**8**) using ethyl acetate for the extraction. The crude product was separated by chromatography on silica gel (13×3.5 cm) using light petroleum (b.p. 40 – 60°C) as eluant to give two fractions: (i) (0.034 g), a mixture of 7-butyl-4,5,6,8,9-pentafluoronaphtho[1,2-c]thiophene (**12**) (5 parts) and 8-butyl-4,5,6,7,9-pentafluoronaphtho[1,2-c]thiophene (**13**) (95 parts) (Found: C, 58.05; H, 3.55%; M^+ , 330. $\text{C}_{16}\text{H}_{11}\text{F}_5\text{S}$ requires C, 58.18; H, 3.36%; M , 330); $\delta_{\text{H}}(\text{CDCl}_3)$ for (**13**): 0.97 (t, CH_3), 1.41 (m, CH_2), 1.66 (m, CH_2), 2.86 (t, CH_2), and 7.75 and 8.34 (both m, unassigned 1-H, 3-H); $\delta_{\text{F}}(\text{CDCl}_3)$ for (**13**): -120.1 (nm, 9-F), -140.5 (d, 7-F), -147.6 (nm, 4-F), -149.3 (dt, 6-F), and -155.4 (dt, 5-F, $J_{5-\text{F},6-\text{F}}$ 62 Hz); $\delta_{\text{F}}(\text{CDCl}_3)$ for (**12**): -124.5 (d, 6-F), -144.7 (t, unassigned), -154.6 (d, 5-F), and two other resonances overlapping in (**12**), $J_{5-\text{F},6-\text{F}}$ ca. 70 Hz; and (ii) 4,5,6,7,8,9-hexafluoronaphtho[1,2-c]thiophene (**11**) (0.103 g, 4.7%) m.p. 106 – 107°C [from light petroleum (b.p. 40 – 60°C)]. (Found: C, 49.6; H, 0.55%; M^+ , 292. $\text{C}_{12}\text{H}_2\text{F}_6\text{S}$ requires C, 49.32; H, 0.69%; M , 292); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.85 (dd) and 8.43 (q, unassigned 1-H, 3-H); $\delta_{\text{F}}(\text{CDCl}_3)$ -140.8 (m, 9-F), -145.3 (dm, 6-F), -146.5 (m, 4-F), -155.2 (ddt, 5-F), -156.8 (m, overlapping 7-F and 8-F), $J_{5-\text{F},6-\text{F}}$ 66 Hz. The oxidation potential of (**11**) was $+1.92$ V (SCE), by cyclic voltammetry. Elution of the column with ethyl acetate gave a residue (2.1 g) which was re-chromatographed on silica using ethyl acetate to give the 2-carbaldehyde derivative (**10**) (1.059 g, 50%) as the major component.

Reactions of 4,5,6,7-Tetrafluorobenzo[c]thiophene (8).—(a) **With dimethyl acetylenedicarboxylate (DMAD).** Compound (**8**) (0.243 g) and DMAD (2 ml) under nitrogen were heated externally with an oil bath initially at 150°C and then maintained at 130°C for 2.5 h. The excess of DMAD was removed *in vacuo* at $30^{\circ}\text{C}/0.003$ mmHg and the residue purified by chromatography on silica gel using CH_2Cl_2 as eluant to give

dimethyl 5,6,7,8-tetrafluoronaphthalene-2,3-dicarboxylate (**14**) (0.314 g, 84%) m.p. 139.5 – 140°C [from toluene–light petroleum (b.p. 60 – 80°C)] (Found: C, 53.1; H, 2.3%; M^+ , 316. $\text{C}_{14}\text{H}_8\text{F}_4\text{O}_4$ requires C, 53.16; H, 2.53%; M , 316); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.99 (s, $2 \times \text{CH}_3$) and 8.46 (s, 1-H, 4-H); $\delta_{\text{F}}(\text{CDCl}_3)$ -143.6 (5-F, 6-F) and -149.7 (6-F, 7-F).

(b) **With tetrafluorobenzene.** Bromopentafluorobenzene (1.70 g, 6.88 mmol) in dry diethyl ether (50 ml) was treated at -70°C with butyl-lithium in hexane (1.58 M; 4.4 ml, 6.92 mmol) and stirred for 3 h. Compound (**8**) (0.26 g, 1.26 mmol) in dry ether (20 ml) was added to the mixture at -70°C , which was warmed to room temperature and left for 18 h. The solution was acidified with sulphuric acid (2 M), extracted with ether, the extracts dried (MgSO_4), and the solvent evaporated. The residue was chromatographed on silica gel using light petroleum (b.p. 60 – 80°C) as eluant to give 1,2,3,4,5,6,7,8-octafluoroanthracene (**15**) (0.082 g, 21%) m.p. 172 – 173°C [from light petroleum (b.p. 60 – 80°C)] (lit.,¹¹ m.p. 137 – 139°C) (Found: C, 52.4; H, 0.65%; M^+ , 322. $\text{C}_{14}\text{H}_2\text{F}_8$ requires C, 52.19; H, 0.63%; M , 322); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.86 (s, 9-H, 10-H); $\delta_{\text{F}}(\text{CDCl}_3)$ -149.3 (1-F, 4-F, 5-F, and 8-F), and 155.8 (2-F, 3-F, 6-F, and 7-F).

(c) **With lithium propane-2-thiolate.** Compound (**8**) (0.18 g, 0.88 mmol) was treated with lithium propane-2-thiolate in THF–hexane (0.195 M; 4.5 ml, 0.875 mmol) at room temperature for 70 h. The solution was diluted with water, extracted with ether, the extracts dried and the solvent evaporated. The crude product (0.23 g) was shown by ^{19}F NMR spectroscopy to contain three components: unchanged compound (**8**) (20%), 4,6,7-trifluoro-5-propan-2-ylthiobenzo[c]thiophene (**16**) (75%)

$[\delta_{\text{H}}(\text{CDCl}_3)$ 1.29 (d, $2 \times \text{CH}_3$), 3.44 (septet, $-\overset{\text{CH}_3}{\text{C}}\text{H}$), 7.79 and 7.88 (unidentified 1-H and 3-H); $\delta_{\text{F}}(\text{CDCl}_3)$ -122.1 (4-F), -141.2 (6-F), and -151.3 (7-F)] and 4,7-difluoro-5,6-bispropan-2-ylthiobenzo[c]thiophene (**17**) [$\delta_{\text{H}}(\text{CDCl}_3)$ 1.29 (d, $2 \times \text{CH}_3$), 3.60 (septet, $-\overset{\text{CH}_3}{\text{C}}\text{H}$), and 7.98 (s, 1-H/3-H); $\delta_{\text{F}}(\text{CDCl}_3)$ -128.7

ppm (s, 4-F/7-F). Chromatography of the mixture on silica gel using light petroleum (b.p. 40 – 60°C) gave unchanged (**8**) and an inseparable mixture of (**16**) and (**17**) which decomposed in air and so prevented their full characterisation.

(d) **With 'magic acid'** ($\text{SbF}_5\text{-HF}$). Compound (**8**) (0.51 g, 2.47 mmol) in CH_2Cl_2 (1 ml) was treated at room temperature with two drops of 'magic acid'. The mixture was stirred at room temperature for 20 h, and the resultant viscous solution diluted with THF and added to methanol. The yellow solid which precipitated was filtered off, re-dissolved in THF, and re-precipitated. The dissolution–reprecipitation cycle was repeated to give poly(1,3-dihydro-4,5,6,7-tetrafluorobenzo[c]thiophene) (**20**) (0.39 g, 77%) (Found: C, 46.5; H, 0.55%; $\text{C}_8\text{H}_2\text{F}_4\text{S}$ requires C, 46.61; H, 0.98%; $\delta_{\text{H}}(\text{CDCl}_3)$ 5.27 (br s), 5.5 (br s), 5.67 (br s); $\delta_{\text{F}}(\text{CDCl}_3)$ -139.1 (br t), 140.9 (br s) and -153.6 (br d); the ratio of the two lowest absorptions to the highest was 1:1. Gel permeation chromatography gave the value of M_n ca. 20 000 (100 repeating units).

Oxidation of (20) to the Poly Sulphone (28).—Polymer (**20**) (0.035 g, 0.17 mmol) in ethyl acetate at 0°C was treated with *m*-chloroperbenzoic acid (0.26 g of 50–55% material, 0.75 mmol). The solution was warmed to room temperature and after 10 min a solid was precipitated. After 50 min the solution was homogeneous and yellow. The solvent was evaporated, the residue dissolved in water, and the solution dialysed using a Visking seamless tube (pore size 24 \AA). Evaporation of the aqueous solution gave a yellow solid (**28**) (0.039 g, 96%) (Found: C, 40.95; H, 0.85. $\text{C}_8\text{H}_2\text{F}_4\text{OS}$ requires C, 40.48; H, 1.61%).

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