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Fluorinated molecules relevant to conducting polymer research

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Abstract

The synthesis of versatile fluorine compounds for conducting polymer research on fluorinated materials is presented. 1,2,4,5-Tetrafluorobenzene was converted to 1,2,4,5-tetrafluorobenzaldehyde (**1**) and protected as an acetal. This gave the acetals 1,2,4,5-tetrafluoro-3-(1,3-dioxol-2-yl)benzene (**2a**) and 1,2,4,5-tetrafluoro-3-(5,5-dimethyl-1,3-dioxan-2-yl)benzene (**2b**). Compounds **2a** and **2b** were converted into the semiprotected 2,3,5,6-tetrafluoroterephthaldehydes: 1,2,4,5-tetrafluoro-3-(1,3-dioxol-2-yl)-6-formylbenzene (**3a**) and 1,2,4,5-tetrafluoro-3-(5,5-dimethyl-1,3-dioxan-2-yl)-6-formylbenzene (**3b**). While **3a** was easily deprotected to give 2,3,5,6-tetrafluoroterephthaldehyde (**4**) compound **3b** proved very resilient to hydrolysis and gave a 1:1 mixture of **4** and 1,2,4,5-tetrafluoro-3,6-bis(5,5-dimethyl-1,3-dioxan-2-yl)benzene (**5**). Compound **4** was reduced to 1,2,4,5-tetrafluoro-3,6-dihydroxymethylbenzene (**6**) and converted into 1,2,4,5-tetrafluoro-3,6-dibromomethylbenzene (**7**). Compound **7** was finally converted into 1,2,4,5-tetrafluoro-3,6-bis(diethylphosponylmethyl)benzene (**8**). Compounds **4** and **8** are versatile fluorinated molecules that can be used to replace their hydrogen counterparts in many molecules and materials. To illustrate this compounds **4** and **8** were oligomerised to give partially fluorinated polyphenylenevinylene (**9**).

Keywords: Versatile tetrafluorobenzene derivatives; Fluorinated monomers; Fluorinated polyphenylenevinylene; Fluorinated conducting polymers

1. Introduction

The literature on the subject of conducting polymers has expanded dramatically within the past 10 years. Particular interest has been devoted to the realisation of polymer based applications [1–3]. Of crucial importance to the proper function and application of these materials are the position of the electronic energy levels [4,5]. In this respect fluorine is particularly attractive due to the strong inductive effect where it is possible to lower the position of the valence band without large alterations in the magnitude of the optical bandgap. Furthermore, large changes in the emission properties upon fluorine substitution have been observed for dye molecules [6,12] and for polytetrafluorophenylenevinylene (FPPV) itself where excellent photoluminescence in a light emitting diode application with low turn-on voltage has been reported [7]. Many of the synthetic procedures however require readily accessible fluorinated materials and detailed reports on versatile synthetic procedures leading to fluorine containing materials are not as preponderant as for the hydrogen containing analogues.

In this paper, we describe the synthesis of a series of versatile fluorinated molecules pertaining to fundamental studies of fluoroorganic compounds. The range of compounds presented are particularly relevant to conducting polymer research. We have exemplified their use in the synthesis of fluorinated oligophenylenevinylene. Structural drawings are shown in Scheme 1.

2. Results and discussion

2.1. Synthesis

Polyparaphenylenevinylene (PPV) [8] the conducting polymer that has proved the most applicable both in terms of device construction and fundamental studies in conducting polymer physics involving theory and experiment. Studies on variations in the PPV backbone and molecular structure are numerous and include reports of a partially halogenated and fluorinated backbone [9,10], the incorporation of tetrafluorophenylene in a copolymer [11] and the use of the tetrafluorophenylenevinylene oligomers to efficiently organise block copolymers with application to electroluminescent devices [12]. We decided to synthesise versatile fluorinated molecules that were suitable for these tasks

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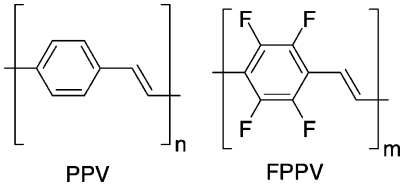


Scheme 1.

starting from simple 1,2,4,5-tetrafluorobenzene as outlined in Scheme 2 employing simple lithiation using *n*BuLi in THF at dry ice temperatures. The formation of the aldehyde is very sluggish when using traditional carbanion formylation reagents (DMF, *N*-methylformamide). We found that excess ethyl formate was the only reagent that gave the aldehyde in moderate yield. The aldehyde was subsequently protected with ethylene glycol by a standard procedure employing azeotropic distillation of water from toluene under acid catalysis giving **2a**. The acetal was easily distilled and could be subjected to a further lithiation following the same procedure as above. The semiprotected dialdehyde **3a** was crystallised to high purity and easily deprotected in warm aqueous trifluoroacetic acid giving the desired fluorinated terephthaldehyde, **4**. The molecules presented in Scheme 2 allow for easy access to unsymmetrical substitution in the 3,6 positions of the 1,2,4,5-tetrafluorobenzene skeleton.

Crystals of compound **4** had a slightly yellow colour even when purified by repeated crystallisation. In comparison terephthaldehyde is colourless and the crystal structure of **4** showed a very similar molecular geometry [13] as shown in Fig. 1.

Compound **4** could be reduced with borane-dimethylsulfide to give the dialcohol **6** as shown in Scheme 3. The conversion of compound **6** into the dibromide **7** using thionylbromide or CBr_4/Ph_3P proved unfruitful. Phosphoroustribromide was found suitable for the reaction.

However, during the reaction a considerable amount of an insoluble orange material was formed and further after removal of excess phosphoroustribromide (by distillation at low pressure) it proved difficult to properly isolate **7** in a pure form. The product could be crystallised from

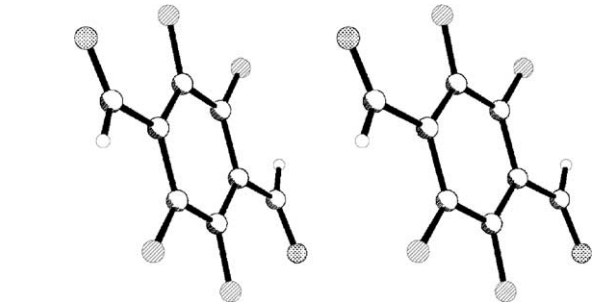


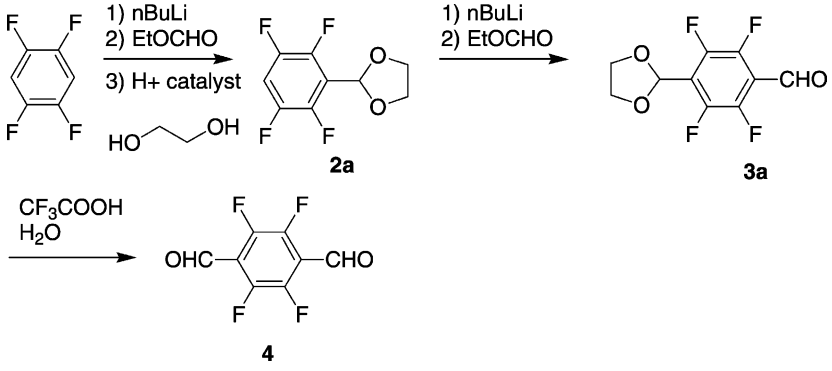
Fig. 1. A stereoview showing the molecular geometry of **4**.

tetrachloroethylene or CCl_4 but the impurities were not efficiently alleviated and this made further reaction difficult. The impurities could be efficiently removed by passing the product mixture dissolved in chloroform through a large excess of silica. The yellow impurities were filtered off in this manner and only the clear colourless chloroform phase was collected and subsequently concentrated to give pure **7**. Compound **7** was converted to the diethylphosphonate ester, **8**, under standard Arbuzov conditions by reflux in excess triethylphosphite. Interestingly **8** was found to be able to crystallise with or without a water molecule as observed by crystal structure solution. The molecular geometry of **8** is shown in Fig. 2.

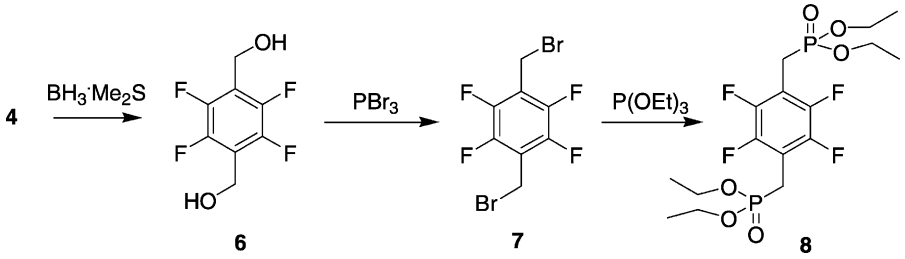
The use of compounds **6** [14], **7** [15] and the methyl analogue of **8** [11,12,16] have been reported in the literature but little synthetic details were given and we therefore present full synthetic detail and analytical data here.

The synthesis of the partially fluorinated PPV oligomer was achieved by reacting the dialdehyde **4** and the diphosphonate ester **8** using NaH as base and dry THF as solvent. The synthesis of the oligomer is shown in Scheme 4.

Compound **9** was obtained as a yellow solid. The material was poorly soluble in THF at 40 °C where the molecular weight determination using solvent exclusion chromatography (SEC) was attempted. The molecular weight obtained from the SEC experiment using polystyrene standards was found to be approximately 1000 g mol^{-1} indicating that the soluble part of the material consist of oligomers. It has to be kept in mind that **9** is likely to have a stiff geometry in



Scheme 2.



Scheme 3.

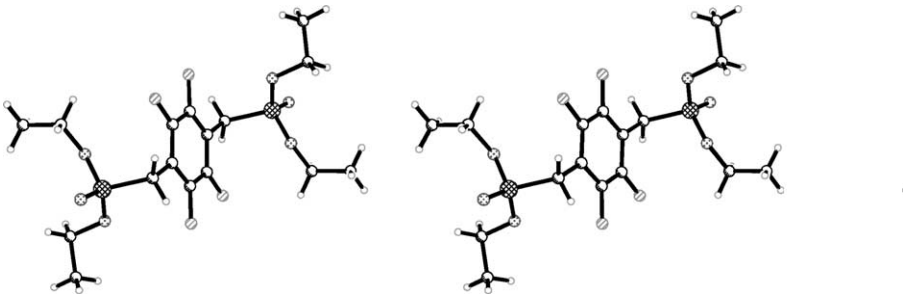
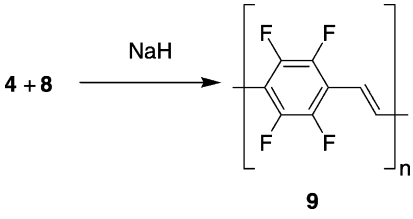


Fig. 2. A stereoview of **8** showing the molecular geometry of the bisphosphonate ester.



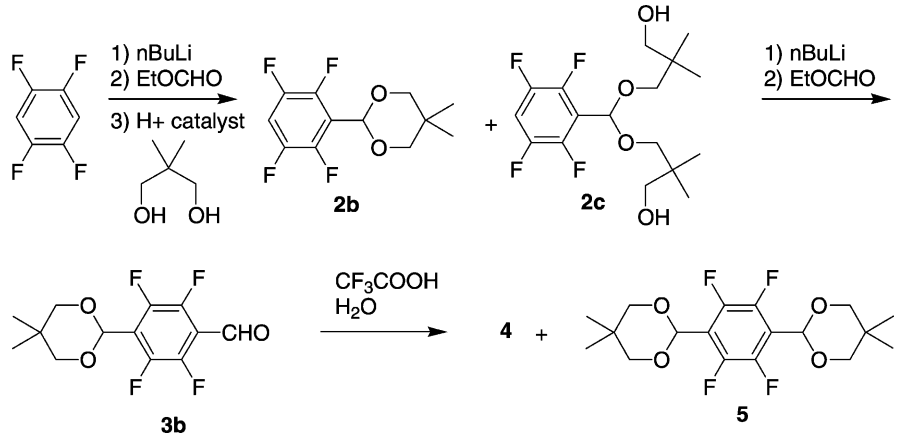
Scheme 4.

solution and that the molecular weight based on the standards is not an absolute but a relative measure depending on the hydrodynamic volume of the standards and the sample. MALDI-TOF showed the presence of molecular weights up to 2200 g mol^{-1} corresponding to the bisphosphonate terminated undecamer. While the true yield and polymeric nature of the product was difficult to establish due to the insolubility of the product our results do show that the formation of oligomers is possible by this reaction.

2.2. Acetal formation

We initially employed neopentylglycol as the protecting diol for the acetal formation shown in Scheme 5. There were some complications that were easily avoided by the use of ethylene glycol as the protecting diol.

Firstly, when using benzene as the solvent for the azeotropic distillation along with an excess of neopentylglycol we obtained, aside from the desired acetal, **2b**, also considerable amounts of the very unexpected 1,2,4,5-tetrafluoro-3-bis(3-hydroxy-2,2-dimethylpropyloxy)methylbenzene, **2c**. The molecular structure of **2c** was confirmed by solving the X-ray structure as shown in Fig. 3. It was found that using toluene as the solvent under vigorous reflux and



Scheme 5.

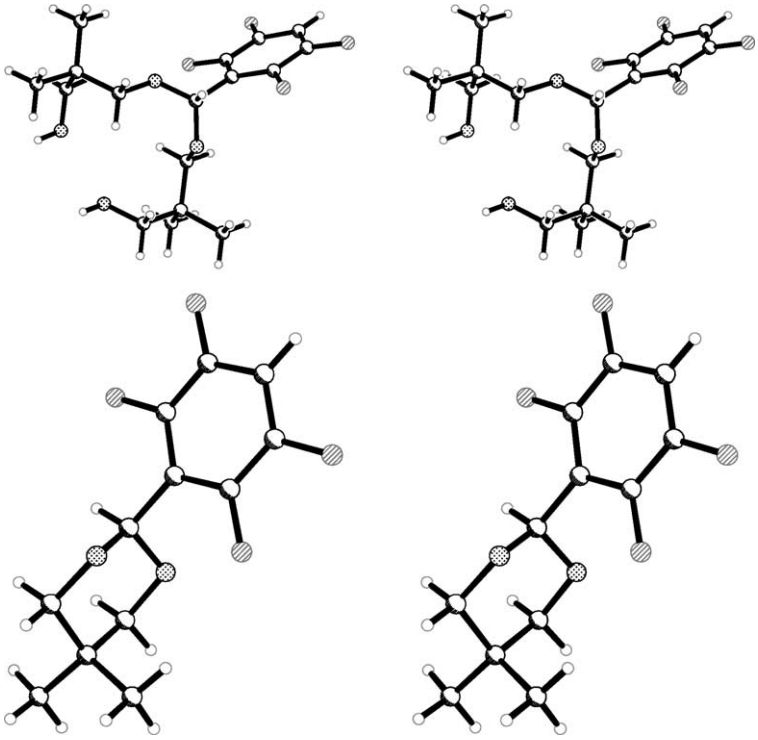


Fig. 3. The molecular structure of the unexpected acetal **2c** as a stereoview (above) and a sterioview of the acetal **2b** showing the molecular geometry in the crystal (below). The geometry explains the ^{1}H NMR spectrum where two different methyl proton signals are seen and a strong geminal coupling of the methylene protons next to oxygen.

only a small excess of neopentylglycol avoided this problem. The reaction was complete in less than 1 h.

2.3. Deprotection

The deprotection, however, proved very difficult as outlined in Scheme 5 where a 1:1 mixture of the desired aldehyde **4** and the doubly protected aldehyde **5** was obtained. In order to find an explanation for the resilience of neopentylglycol derived acetals to strongly acidic aqueous conditions the crystal structure was solved to determine the geometry of the acetal **2b**. The molecular structure is shown in Fig. 3 showing how the steric effect of the fluorine atoms forces the angle formed between the plane of the benzene ring and the mean plane of the dioxane ring to be near 90°.

Unfortunately there have been no previous reports on the crystal structure of an acetal made from an aromatic aldehyde and neopentylglycol. Further, only 24 structures (at present) containing an acetal of an aromatic aldehyde with a 2,2-disubstituted 1,3-propanediol have been reported making a statistically justified comparison difficult though the data does indicate that a torsion angle of around 90° as observed here is preferred. From this point of view, it would seem that the reason for the difficulty encountered in the hydrolysis is not a steric one. A likely reason is the inductive electron withdrawing effect of the fluorine atoms that destabilises any protonated and formally positively charged intermediate.

3. Conclusion

We have presented a versatile synthetic approach giving access to multigram quantities of symmetrically and asymmetrically 3,6-disubstituted 1,2,4,5-tetrafluorobenzene derivatives. We identified important problems in the acetal formation and deprotection of the formyl derivatives and showed by crystal structure solution the nature of the by-products that formed when using neopentylglycol as the protecting diol. Furthermore the neopentylglycol acetals were difficult to deprotect. The problems were easily and effectively avoided simply using ethyleneglycol as protecting diol. Our work is particularly relevant to fluorinated materials with emphasis on conducting polymers and oligomers. We succeeded in applying the precursors for the synthesis of partially fluorinated oligoparaphenylenevinylene.

4. Experimental

All chemicals were reagent grade. NMR spectra were recorded on a 250 MHz instrument at 300 K unless otherwise stated. TMS was used as reference in the ^{1}H NMR spectra and C_6F_6 in a sealed capillary was used as a standard for the ^{19}F NMR spectra. Melting points are uncorrected. SEC was performed using THF as the eluent at 40 °C using polystyrene standards for calibration. MALDI-TOF was performed with negative ion detection.

4.1. 1,2,4,5-Tetrafluoro-3-(1,3-dioxol-2-yl)benzene (**2a**)

A dry 2-l three necked flask under argon containing dry THF (1000 ml) was cooled to −78 °C. *n*BuLi (340 ml, 1.6 M, 0.54 mol) was added and the mixture cooled to −78 °C. 1,2,4,5-Tetrafluorobenzene (80 g, 0.53 mol) was added slowly. The reaction is exothermic and the temperature was kept below −50 °C. The colour remained light yellow until the end of the addition where the mixture became colourless and a white precipitate formed. After 1 h ethyl formate (80 g, excess) was added in one portion. The precipitate dissolved and the mixture was allowed to reach room temperature. The mixture was washed with saturated $NaHCO_3$(aq) (200 ml). The organic phase was separated, dried with $MgSO_4$, filtered and the solvent was removed in vacuo. The residue was transferred to a 1000 ml conical flask containing ethylene glycol (65.4 g, excess) and toluene (500 ml). *para*-Toluenesulfonic acid (0.6 g, catalyst) was added and the mixture refluxed with a water separator. The reaction was complete in 2 h. After cooling the mixture was washed with saturated $NaHCO_3$(aq) (200 ml), dried with $MgSO_4$ and evaporated to give an oil that was distilled at 65 °C/1 mmHg. This gave **2a** as a colourless oil that crystallise upon standing in 75% yield (89 g). The mp 37–38 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ 3.98–4.06 (2H, m), 4.18–4.27 (2H, m), 6.24 (1H, s), 7.01–7.14 (1H, m); ^{13}C NMR (63 MHz, $CDCl_3$, TMS): $\delta = 66.7$ (s), 97.5 (m), 107.4 (t, $J = 23$ Hz), 118.6 (t, $J = 12$ Hz), 145.7 (dm, $J = 257$ Hz), 146.4 (dm, $J = 249$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -141.2$ (2F, m), −135.8 (2F, m). Anal. calcd. for $C_9H_6F_4O_2$: C, 48.66; H, 2.72. Found: C, 48.47; H, 2.48.

4.2. 1,2,4,5-Tetrafluoro-3-(5,5-dimethyl-1,3-dioxan-2-yl)benzene (**2b**)

The raw aldehyde solution in toluene was prepared as described for **2a** above. 2,2-Dimethylpropane-1,3-diol (37 g, excess) and *para*-toluenesulfonic acid (0.5 g, catalyst) was added and the mixture was refluxed vigorously with a water separator for 1 h. The water separation is very fast initially. The mixture was cooled and NaOH(aq) (200 ml, 1 M) was added and the mixture further washed with water (3 × 1 l). The organic phase was dried using $MgSO_4$ and evaporated to give an oil that was distilled at 142–143 °C/17 mmHg. This gave **2b** as a colourless material in 75% yield (67 g). The mp 50–51 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.81$ (3H, s), 1.37 (3H, s), 3.62 (2H, d, $J = 11$ Hz), 3.77 (2H, d, $J = 10$ Hz), 5.80 (1H, s), 6.99–7.13 (1H, m); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 22.3$ (s), 23.4 (s), 31.1 (s), 78.6 (s), 95.7 (m), 107.2 (t, $J = 23$ Hz), 118.4 (t, $J = 14$ Hz), 145.4 (dm, $J = 253$ Hz), 146.7 (dm, $J = 252$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -139.4$ (2F, m), −135.8 (2F, m). Anal. calcd. for $C_{12}H_{12}F_4O_2$: C, 54.55; H, 4.58. Found: C, 54.52; H, 4.49.

4.3. 1,2,4,5-Tetrafluoro-3-bis(3-hydroxy-2,2-dimethylpropyloxy)methylbenzene (**2c**)

The raw aldehyde was prepared as described for **2a** above. The raw aldehyde was extracted with benzene (750 ml) and dried using $MgSO_4$. 2,2-Dimethylpropane-1,3-diol (60 g, excess) and *para*-toluenesulphonic acid (0.5 g, catalyst) was added and the mixture was refluxed gently with a water separator for 72 h. The mixture was cooled and NaOH(aq) (200 ml, 1 M) was added. The mixture was further washed with water (3 × 1 l). The organic phase was dried using $MgSO_4$ and evaporated to give an oil that was distilled. The fraction boiling at temperatures up to 190 °C/17 mmHg was mainly **2b**. The remaining compound was distilled with an oil pump and the fraction boiling at 152–154 °C/1 mmHg was collected as a material that solidifies. This gave **2c** as a colourless material in 12% yield (14.7 g). The mp 70–71 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.91$ (6H, s), 0.92 (6H, s), 2.35 (2H, bs), 3.32–3.57, (8H, m), 5.73 (1H, s), 7.00–7.14 (1H, m); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 21.58$ (s), 21.63 (s), 36.3 (s), 69.5 (s), 74.4 (s), 97.2 (m), 106.2 (t, $J = 14$ Hz), 117.8 (m), 144.4 (dm, $J = 251$), 145.9 (dm, $J = 248$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -139.7$ (2F, m), −135.1 (2F, m). Anal. calcd. for $C_{17}H_{24}F_4O_4$: C, 55.43; H, 6.57. Found: C, 55.53; H, 6.52.

4.4. 1,2,4,5-Tetrafluoro-3-(1,3-dioxol-2-yl)-6-formylbenzene (**3a**)

Compound **2a** (95 g, 0.43 mol) was dissolved in dry THF (1000 ml) and cooled to −78 °C. *n*BuLi (280 ml, 1.6 M, 0.45 mol) was added quickly while keeping the temperature below −25 °C. When the temperature stopped rising ethyl formate (64.6 g, excess) was added and the mixture became light yellow. After the addition the mixture was allowed to reach room temperature and saturated aqueous $NaHCO_3$ (200 ml) was added to give a two phase system. The organic phase was separated, dried with $MgSO_4$ and the solvent was removed using a rotary evaporator. The crude product was recrystallised from *n*-heptane (1000 ml). This gave **3a** as a colourless material in 76% yield (81 g). The mp 76–78 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 4.01-4.22$ (4H, m), 6.21 (1H, s), 10.27 (1H, s); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 66.9$ (s), 97.1 (s), 116.2 (t, $J = 10$ Hz), 123.8 (t, $J = 13$ Hz), 145.8 (dm, $J = 250$ Hz), 147.2 (dm, $J = 257$ Hz), 182.9 (s); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -142.2$ (2F, m), −139.9 (2F, m). Anal. calcd. for $C_{10}H_6F_4O_3$: C, 48.01; H, 2.42. Found: C, 48.26; H, 2.22.

4.5. 1,2,4,5-Tetrafluoro-3-(5,5-dimethyl-1,3-dioxan-2-yl)-6-formylbenzene (**3b**)

Compound **2b** (67 g, 0.26 mol) was dissolved in dry THF (500 ml) under Ar and cooled to −78 °C. *n*BuLi (1.7 M, 160 ml, 0.27 mol) was added in three equal portions allowing

the temperature to decrease below −60 °C between successive portions. The reaction is exothermic and the colour changes to light red. After stirring for 15 min ethyl formate (150 ml, excess) was added in one portion and the mixture allowed to reach room temperature. NH_4Cl(aq) (2 M, 500 ml) was added and the organic phase separated, washed with water, dried and evaporated to give a solid. The solid was recrystallised from heptane (250 ml) by extended heating. After crystallisation the product was filtered, washed with light petrol and dried overnight in the vacuum oven at 50 °C. This gave **3b** as colourless needle shaped crystals in 73% yield (56 g). The mp 116–117 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.80$ (3H, s), 1.34 (3H, s), 3.61 (2H, d, $J = 11$ Hz), 3.77 (2H, d, $J = 11$), 5.80 (1H, s), 10.28 (1H, s); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 22.3$ (s), 23.4 (s), 31.2 (s), 78.6 (s), 95.3 (m), 116.1 (t, $J = 10$ Hz), 123.1 (t, $J = 14$ Hz), 145.5 (dm, $J = 252$ Hz), 147.2 (dm, $J = 256$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -142.0$ (2F, m), −137.7 (2F, m). Anal. calcd. for $C_{13}H_{12}F_4O_3$: C, 53.43; H, 4.14. Found: C, 53.59; H, 4.18.

4.6. 2,3,5,6-Tetrafluoroterephthaldehyde (*4*)

Trifluoroacetic acid (200 ml, excess) was placed in a conical flask. Compound **3a** (83 g, 0.33 mol) was added slowly giving a yellow mixture, followed by water (1000 ml) and hydrochloric acid (200 ml, 37%). A precipitate form during the addition. After 20 min stirring at 55 °C the mixture was allowed to reach RT. The solution was extracted with chloroform (3 × 500 ml) and the organic phase was isolated. The organic phase was washed with water (500 ml) and the solvent was removed in vacuo to give a light yellow and solid product. The product was recrystallised from chloroform (600 ml). This gave **4** as light yellow and needled shaped crystals in 72% yield (49 g). The mp 131–132 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 10.33$ (2H, s); ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 119.6$ (s), 147.2 (dm, $J = 265$ Hz), 182.1–182.2 (m); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -140.8$ (4F, s). Anal. calcd. for $C_8H_2F_4O_2$: C, 46.62; H, 0.98. Found: C, 46.79; H, 0.79.

4.7. 1,2,4,5-Tetrafluoro-3,6-bis(5,5-dimethyl-1,3-dioxan-2-yl)benzene (*5*)

Compound **3b** (10 g, 34 mmol) was dissolved in trifluoroacetic acid (100 ml) and heated to reflux. Water (25 ml) was added and the mixture was refluxed for 1 h. Water (175 ml) was added and the mixture refluxed for 1 h during which a solid starts to precipitate. The mixture was cooled and filtered. The solid was washed with water, dried and recrystallised from heptane (compound **4** (3 g, 43%) could be recovered from the liquor by evaporation). This gave **5** as colourless needle shaped crystals in 47% yield (6.1 g). The mp 169–170 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.80$ (6H, s), 1.36 (6H, s), 3.60 (4H, d, $J = 11$), 3.77 (4H, d, $J = 11$), 5.78 (2H, s); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 22.4$ (s), 23.5 (s), 31.1 (s), 78.6 (s), 95.6 (m), 145.4 (dm, $J = 247$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -139.4$ (4F, s). Anal. calcd. for $C_{18}H_{22}F_4O_4$: C, 57.14; H, 5.86. Found: C, 57.34; H, 5.91.

4.8. 1,2,4,5-Tetrafluoro-3,6-dihydroxymethylbenzene (*6*)

Compound **4** (40 g, 0.20 mol) was dissolved in dry THF (1000 ml) under Ar and cooled to 0 °C. The mixture was light yellow. $(CH_3)_2S{\cdot}BH_3$ was added slowly keeping the temperature below 5 °C. During the addition of $(CH_3)_2S{\cdot}BH_3$ the mixture became colourless. After the addition the mixture was kept at 0 °C for 15 min and then allowed to reach RT. Methanol (750 ml) was added carefully due to the vigorous development of H_2. When the development of H_2 had ceased (approximately 45 min) the solvent was removed using a rotary evaporator. The product was recrystallised from toluene (600 ml). This gave **6** as a colourless material in 83% yield (34 g). The mp 126–127 °C; ^{1}H NMR (250 MHz, Me_2SO, 300 K, TMS): $\delta = 4.58$ (4H, d, $J = 5$ Hz), 5.53 (2H, t, $J = 6$ Hz); ^{13}C NMR (63 MHz, Me_2SO, 300 K, TMS): $\delta = 38.5–40.5$ (m), 50.86–50.93 (m), 118.9–119.5 (m), 144.2 (dm, $J = 252$ Hz); ^{19}F NMR (235 MHz, Me_2SO, 330 K, C_6F_6): $\delta = -141.8$ (4F, s). Anal. calcd. for $C_8H_6F_4O_2$: C, 45.73; H, 2.88. Found: C, 45.71; H, 2.73.

4.9. 1,2,4,5-Tetrafluoro-3,6-dibromomethylbenzene (*7*)

Compound **6** (34 g, 0.16 mol) was heated gently with PBr_3 (75 ml, 97%, excess) for 1 h. The mixture was distilled at a pressure of 17 mmHg by heating on an oil bath kept at 100 °C. During the reflux an orange sticky precipate formed. When the distillation of the excess PBr_3 had ceased the contents of the distillation flask were cooled and the system repressurised with argon (CAUTION! letting air into the system at this point occasionally lead to ignition. We ascribe this to the formation of low oxidation states of phosphor during the reaction). The residue was dissolved in chloroform (1 l) and silica (500 g) was added slowly (CAUTION! the mixture reacts with the silica providing considerable amounts of HBr). When the reaction had subsided the slurry was poured onto a column containing silica (250 g). The column was washed with chloroform (4 × 500 ml) collecting only the clear fractions of $CHCl_3$. The solvent was removed using the rotary evaporator leaving **7** as a colourless material which was recrystallised from CCl_4 (400 ml). This gave **7** as a colourless material in 63% yield (34 g). The mp 125–126 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 4.51$ (4H, s); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 16.8$ (m), 118.0 (m), 145.3 (dm, $J = 254$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -139.0$ (4F, s). Anal. calcd. for $C_8H_4Br_2F_4$: C, 28.60; H, 1.20. Found: C, 28.35; H, 1.07.

4.10. 1,2,4,5-Tetrafluoro-3,6-bis(diethylphosponylmethyl)benzene (8)

Compound **7** (10 g, 30 mmol) was added to boiling triethylphosphite (100 ml, excess) and Ar was bubbled through the mixture. During the additon the mixture became light green. The mixture was kept at the boiling point for 15 min and then cooled to room temperature. The last traces of the mixture of triethylphosphate, ethyldiethylphosphonate and triethylphosphate was removed with an oil pump. The residue crystallised giving a colourless product. The product was recrystallised from *n*-heptane (150 ml). This gave **8** as a colourless material in 82% yield (11 g). The mp 41–42 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 1.22$ (12H, t, $J = 7$), 3.18 (4H, d, $J = 20$ Hz), 4.01–4.07 (8H, m); ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 16.0$ (m), 21.4 (d, $J = 142$ Hz), 62.5 (m), 110.6 (m), 144.7 (dm, $J = 243$ Hz); ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -139.0$ (4F, s). Anal. calcd. for $C_{16}H_{24}F_4O_6P_2$: C, 42.68; H, 5.37. Found: C, 42.68; H, 5.34.

4.11. Poly-(2,3,5,6-tetrafluoro-1,4-phenylene-1,2-vinylene) (9)

Compound **8** (1.13 g, 2.5 mmol) was placed in a conical flask and dissolved in THF (500 ml). NaH (60%, 0.5 g, excess, washed with *n*-hexane) was added and the mixture was stirred for 20 min. Subsequently compound **4** (0.52 g, 2.5 mmol) was added. This turned the colour of the mixture from dark green to brown with blue flourescence. The mixture was refluxed under argon over night. Afterwards CH_3OH (500 ml) and HCl (3 ml, 37%) was added changing the colour of the mixture from brown to yellow. The solvent was removed in vacuo. This gave compound **9** as a yellow powder. The powder was washed with CH_2Cl_2 (200 ml) and CH_3OH (200 ml). This gave **9** as a yellow material in 58% yield (0.26 g).

4.12. Crystallography

General crystallographic data for **2b**, **2c**, **4** and **8** can be found in Table 1. The crystals were mounted on a glass capillary using Apiezon™ grease and transferred to the cold stream on the diffractometer.

An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames; each set with a different φ angle for the crystal and each frame covering a scan of 0.3° in ω. Data collection, integration of frame data and conversion to intensities corrected for Lorenz, polarization and absorption effects were performed using the programs SMART [17], SAINT [17] and SADABS [18]. Structure solution, refinement of the structures, structure analysis and production of crystallographic illustrations was carried out using the programs SHELXS97 [19], SHELXL97 [19] and SHELXTL [20]. The structure was checked for higher symmetry and none was found [21]. The H atoms were included in their calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-191096, CCDC-191097, CCDC-191098 and CCDC-191099. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystallographic data for the compounds **2b**, **2c**, **4** and **8**

	Compounds			
	2b	**2c**	**4**	**8**
Formula	$C_{12}H_{12}F_4O_2$	$C_{17}H_{24}F_4O_4$	$C_8H_2F_4O_2$	$C_{16}H_{24}F_4O_6P_2{\cdot}H_2O$
Formula wt.	264.22	368.36	206.10	468.31
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1	$P2_1/n$	P-1
Type of radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Z	8	2	2	2
a (Å)	23.356(4)	6.0397(14)	7.6258(11)	7.9527(14)
b (Å)	5.5606(9)	11.300(3)	5.6926(9)	9.5390(17)
c (Å)	19.572(3)	13.802(3)	8.2861(13)	14.899(3)
α (°)	90	68.329(4)	90	93.421(3)
β (°)	113.649(3)	82.626(4)	103.594(3)	98.848(3)
γ (°)	90	89.237(5)	90	106.888(3)
V (Å^3)	2328.4(7)	867.6(4)	349.63(9)	1062.1(3)
ρ (g cm^3)	1.507	1.410	1.958	1.464
Crystal dimensions (mm)	0.83 × 0.75 × 0.50	0.25 × 0.16 × 0.10	0.75 × 0.70 × 0.25	0.76 × 0.50 × 0.25
μ (cm^{-1})	0.143	0.126	0.208	0.274
T (K)	120(2)	120(2)	120(2)	120(2)
Number of reflections	28199	11470	4179	13506
Unique reflections ($I > 2\sigma$)	4018	4756	951	5591
R(F), R_w(F^2) all data	0.0551, 0.1678	0.0817, 0.2678	0.0385, 0.0971	0.0383, 0.1194

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