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POLYFLUORINATED HETEROCYCLIC COMPOUNDS. PART 29[1]. THE SYNTHESIS OF 4,5,6,7,8-PENTAFLUORO-2H-CYCLOHEPTA[b]FURAN-2-ONE AND ITS REACTION WITH SODIUM METHOXIDE.

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SUMMARY

Pentafluorophenyl propynoate (8), prepared from sodium pentafluorophenate and propynoyl chloride, on flash vacuum pyrolysis through silica gave 4,5,6,7,8-pentafluoro-2Hcyclohepta[b]furan-2-one (9). Treatment of (9) with sodium methoxide in methanol at -70°C produced a mixture of the 4-methoxy-, 5-methoxy-, 6-methoxy-, 7-methoxy- and 8-methoxy-tetrafluoro-2H-cyclohepta[b]furan-2-one compounds (10), (11), (12), (13) and (14) in the ratio 11:18:8:19:44 respectively. Under more forcing conditions, the 4,8- and 5,8-dimethoxy-trifluoro-2H-cyclohepta[b]furan-2-one compounds (15) and (16) respectively were formed. X-ray crystallography identified the 8-methoxy derivative (14), whose fluorine nmr spectrum enabled key resonances to be identified in the parent (9) and subsequently allowed the structures of all the other products to be deduced.

INTRODUCTION

Two strategically different syntheses of octafluorotropilidene (1) have been described in the literature [2,3]. The first [2] involved a multi-stage process starting

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with the reaction of cycloheptane [4] or cyclohepta-1,3,5-triene [2] with cobalt trifluoride while the second [3] involved an initial photochemical isomerisation of octafluoronorbornadiene (2) followed by two consecutive thermal isomerisation reactions. The norbornadiene compound (2) has been prepared from hexafluorocyclopentadiene [5] and more recently a synthesis starting from the Dewar benzene (3) has been published [6]. Removal of fluoride ion from the CF₂ group of (1) with boron trifluoride etherate gave the 6π electron species (4), which with water was converted into hexafluorotropone (5) [3]. The first synthesis of (5) by the simple hydrolysis of (1) had been reported earlier [7].

We were interested in exploring short alternative routes to highly conjugated perfluorinated derivatives of the cycloheptane ring system starting from readily available fluoroaromatic compounds and a recent review [8] drew our attention to some work by Trahanovsky in 1976 involving the conversion of phenyl propynoate(6) to 2H-cyclohepta[b]furan-2-one (7) by flash vacuum pyrolysis (FVP) [9] (Scheme 1). This reaction was an ideal candidate for application to the pentafluorophenyl analogue.



Scheme 1.

RESULTS AND DISCUSSION

Pentafluorophenyl propynoate (8) was prepared by treating sodium pentafluorophenate in water with propynoyl chloride [10] in light petroleum. Flash vacuum pyrolysis of the ester (8) through a silica tube packed with short pieces of silica tubing at 640° C/0.01 mm gave a very dark product from which a golden yellow solid, 4,5,6,7,8-pentafluorocyclohepta[b]furan-2-one (9) (8%) was separated by flash chromatography. The structure of the product (9) was presumed to be the fluorine containing analogue of (7) by its colour, and an X-ray crystallographic analysis on a tetrafluoro-monomethoxy derivative (see later) confirmed the expansion of the aromatic ring in (8) to the cycloheptane derivative. The mechanism of the reaction, originally considered by Trahanovsky to be initiated by a 3,3-sigmatropic rearrangement [9], is now thought to proceed via an acetylene-methylene carbene rearrangement [11], as shown applied to the ester (8) in Scheme 2.



Scheme 2.

It was of interest to study the reaction of compound (9) with nucleophiles since both fluorine displacement and/or ring-opening of the lactone ring could occur. The crude product from the reaction with sodium methoxide in methanol at -70° C over 14 min., was examined by ¹⁹F nmr spectroscopy which showed that only fluorine replacement had taken place and to the extent of 22%. Every absorption in the spectrum was subsequently

accounted for by the presence of all the five possible tetrafluoromonomethoxy derivatives from the parent compound (9). The product consisted of the 4-methoxy compound (10), the 5-methoxy compound (11), the 6-methoxy compound (12), the 7-methoxy compound (13), and the 8-methoxy compound (14), present in the ratio 11:18:8:19:44 respectively (Scheme 3).



Scheme 3.

The combined products from five similar reactions and one conducted at room temperature, were subjected to flash chromatography. A mixture of (11), (12) and (13) present in the ratio 33:15:52 was obtained of analytical purity; compound (14) was obtained pure; and compound (10) was identified in a fraction containing the other four monomethoxy derivatives [fraction 8; see EXPERIMENTAL]. The slowest moving material from the chromatography experiment was an analytically pure mixture of two trifluoro-dimethoxy-2H-cyclohepta[b]furan-2-ones: the 4,8-dimethoxy compound (15) and the 5,8-dimethoxy compound (16), present in the ratio of 26:74 respectively.



The structures of all the methoxy-substituted compounds were determined by 19 F nmr spectroscopy in conjunction with the crystal structure of one methoxy derivative, namely compound (14). The 19 F nmr spectrum of the parent pentafluoro compound (9) has a unique doublet at -134.2 ppm and a quartet at -141.6 ppm (all the other three fluorines are fairly complex multiplets). Consequently the fluorine with the doublet structure must be adjacent to one of the two ring fused sites, and provides the third major coupling to the adjacent fluorine to give it the quartet structure. The structure of the one chromatographically pure compound was shown by X-ray crystallography to be the 8-methoxy derivative(14) (see EXPERIMENTAL); its 19 F nmr spectrum did <u>not</u> show a doublet: each fluorine was a complex multiplet. Clearly, the <u>doublet</u> at -134.2 ppm in the parent compound (9) is due to F-8 [since it is missing in (14)] and the quartet at -141.6

In the mixture containing three monomethoxy derivatives, the major component (present to the extent of 52%) has a <u>singlet</u> at -126.8 ppm which must be F-8 with the methoxy group necessarily being at position 7 and so is structure (13). Methoxy group substitution at position 7 can be seen to have caused a substituent chemical shift (SCS) of +7.4 ppm on F-8 in the parent compound (9) [-126.8-(-134.2)].

In polyfluoroaromatic compounds, the SCS of a methoxy substituent varies from <u>ca.</u> +3 to +5.7 ppm for ortho fluorine and -1.5 to -2.0 ppm for meta fluorine; it is -1.7 ppm for the para fluorine in pentafluoroanisole [12]. No outstandingly large SCS values are observed. Re-examining the ¹⁹F nmr spectrum of (14), the absorption at -134.7 ppm is now assigned to F-7 since the adjacent methoxy group gives an entirely satisfactory SCS of +6.9 ppm [-134.7-(-141.6)] (the absorptions at -126.4, -139.2 and -146.9 ppm would have required SCS values of +15.2, +2.4 and -5.3 ppm respectively, all of which are of unreasonable magnitude or sign).

In the mixture containing three monomethoxy derivatives, the compound present to the extent of 33% has a doublet at -135.0 ppm which must be due to F-8; similarly the compound present to the extent of 15% has a doublet at -133.1 ppm which must also be due to F-8. The fifth monomethoxy compound found in fraction 8 from the chromatography experiment has a doublet at -136.0 ppm which again must be due to F-8.

Having assigned the absorptions at F-7 and F-8 in 4,5,6,7,8-pentafluorocyclohepta[b]furan-2-one (9), six assignments of the other three absorptions are possible. Similarly, in all the tetrafluoromonomethoxy compounds in which the absorption at F-8 is known there are also six possible assignments of the other three fluorine absorptions. Taking as an example the monomethoxy derivative present to the extent of 33% in the three component mixture (it could be the 4-, 5-, or 6-methoxy compound), we have carefully examined all six possible fluorine assignments with the methoxy group in position 6 and looked at the SCS values of pseudo-ortho and pseudo-meta fluorines for each of the six possible assignments of the fluorine in the parent pentafluoro compound (9), i.e. 36 possibilities have been examined. No satisfactory SCS values were forthcoming, so the 6-OMe structure was rejected for this component. The exercise was repeated for the methoxy group at position 5 when two of the six possible assignments in (9) gave satisfactory SCS values (including those for a pseudo-para fluorine). With the methoxy group at position 4, one assignment pattern in (9) (different from the ones just mentioned) gave satisfactory SCS values (including two possible pseudo-para fluorines). Clearly, in isolation, these assignments are not unequivocal, but we carried out the analyses in a similar manner for all the other monomethoxy compounds and the two dimethoxy compounds and have found that only one assignment of the fluorines in the pentafluoro compound (9) (see EXPERIMENTAL) gives consistently reasonable SCS shifts for the MeO group when this is present in the positions shown in

compounds (10) to (16): in compounds (11) to (14) the SCS of MeO at a pseudo-ortho site lies in the region +6.5 to +7.6 ppm; at a pseudo-meta site from -1.6 to +1.1 ppm; and at a pseudo-para -0.8 to -1.7 ppm. However in the 4-methoxy compound (10) the SCS at the pseudo-ortho site (F-5) is smaller (+2.1 ppm), at the pseudo-meta site it is 0 ppm and at the pseudo-para sites it is -1.8 ppm (for F-8) and -4.0 ppm (for F-7) (which is quite large). When the SCS values caused by the 4-methoxy group in (10) and those caused by the 8-methoxy group in (14) are considered <u>additively</u>, the SCS values and the shifts of the fluorines expected in the 4,8-dimethoxy compound [(15)-expected] are in excellent agreement with the observed data [(15)-found], Scheme 4.



All unmarked bonds are to fluorine. Chemical Shifts are in CDCl 3 Substituent Chemical Shifts are in brackets.

Scheme 4.

Tatlow and co-workers have published chemical shift data for the ¹⁹F nmr of hexafluorotropone (5) in CDCl_3 , the 2-methoxy- and 3-methoxy-pentafluorotropones (17) and (18) respectively in $(\text{CD}_3)_2$ CO and the 4-methoxypentafluorotropone (19) in CDCl_3 and are shown in Scheme 5 [13]. The SCS value of MeO at a pseudo-ortho site lies in the



All unmarked bonds to fluorine. Chemical Shifts and Substituent Chemical Shifts (in brackets).

Scheme 5.

region +4.7 to +7.4 ppm; at a pseudo-meta from -2.5 to +1.0 ppm, and at a pseudo-para site from -1.3 to -4.0 ppm. Because Tatlow et al. used two solvents in their nmr measurements, direct comparisons between our data and their data are expected to be less than accurate <u>but</u> the particularly large SCS caused by the 4-methoxy group at the pseudo para site in (10) (-4.0 ppm at F-7) is <u>exactly</u> the same as that caused by the 2-methoxy group at the pseudo-para site in (17) (-4.0 ppm at F-5).

The major product from the reaction of hexafluorotropone (5) with sodium methoxide is the 3-methoxy compound (18) accompanied by small amounts of the 4-methoxy compound (19) and 3,6-dimethoxytetrafluorotropone [13]. Nucleophilic attack at the 3-(6-) position in (5) can be rationalised by invoking the Wheland intermediate (20) in which the negative charge is delocalised onto the oxygen of the carbonyl group, but it is not obvious why attack at the 4-position via (21) should be so disfavoured. In a simplistic



way, the remote carbonyl at position 2- in 4,5,6,7,8-pentafluoro-2Hcyclohepta[b]furan-2-one (9) described in this paper <u>is</u> presumably responsible for permitting <u>every</u> fluorine site in the seven membered ring to be attacked. Reaction at positions 4-, 6- and 8- give Wheland intermediates typified by (22) (for attack at the 6-position), while attack at positions 5- and 7- give Wheland intermediates exemplified by (23) (for attack at the 7-position). What is clear from the present work is that the fluorines in the cycloheptatriene ring in (9) are <u>all</u> very reactive, whereas in the tropone (5), the fluorines at the 3- and 6-positions are preferentially replaced [7,13].

EXPERIMENTAL

Nmr spectra were obtained with a Bruker AC250 [1 H (250 MHz) and 19 F (235 MHz). Chemical shifts are positive up-frequency (downfield) from TMS and CFCl₃, 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 unless chemical ionisation (CI) is stated.

Reaction of propynoyl chloride[10] with sodium pentafluorophenate

Propynoic acid (10.5 g) was added to phosphorus pentachloride (33.3 g) at 0°C. The mixture was stirred overnight at room temperature and distilled at room temperature at 0.05 mmHg. The distillate was dissolved in light petroleum (bp 40-60°C) (30 ml) at -15° C and shaken with water at 0°C. This process was repeated twice and the organic phase was added to a solution of pentafluorophenol (31.8 g) dissolved in water (50 ml) containing sodium hydroxide (7.0 g) cooled externally by an ice bath. After being stirred overnight at room temperature, the organic phase was separated, washed with aqueous sodium hydroxide (2M), dried (MgSO₄) and solvent evaporated to give the crude product (17.3 g, 49% based on propynoic acid). Recrystallisation from light petroleum (bp 40-60°C) gave pentafluorophenyl propynoate (nc) (8) m.p. 57.5-59°C (Found: C, 45.61; H, 0.34%; M⁺, 236. C₉HF₅O₂ requires C, 45.78; H, 0.43%; M, 236) $\delta_{\rm F}$ (CDCl₃) -162.1 (3-F/5-F), -156.9 (4-F) and -152.4ppm (2-F/6-F); $\delta_{\rm H}$ (CDCl₃) 3.26ppm (-C=C-<u>H</u>); $\nu_{\rm max}$ 3280 (=C-H), 2130 (C=C).

The pyrolysis of pentafluorophenyl propynoate(8). Isolation of 4,5,6,7,8-pentafluoro-2H-cyclohepta[b]furan-2-one (9)

The ester (8) (4.21 g) was sublimed over 20 min. through a pyrex pyrolysis tube 30 cm x 2 cm diameter packed with 6 mm lengths of 6 mm silica tubing, at 640° at a pressure of 0.01 mmHg. The crude product (3.41 g) was separated by flash chromatography on silica gel (6" x 2" diameter) using a mixture of CCl₄ and CHCl₃ (1:1 v/v) to give three fractions: fraction 1 (2.17 g) was largely unreacted ester (8); fraction 2 (0.08 g) was not examined; and fraction 3 (0.329 g, 8%) a bright yellow solid, was impure (9). Samples of this coloured material from several experiments were combined and further purified by sublimation at 60° C/0.05 mmHg. Recrystallisation from light petroleum (bp $60-80^{\circ}$ C) gave 4.5.6.7.8-pentafluoro-2H-cyclohepta[b]furan-2-one (nc) (9) mp 88.5-89.5°C (Found: C, 45.84; H, 0.38%; M⁺, 236. C₉HF₅O₂ requires C, 45.78; H, 0.43%; M, 236)

$$\begin{split} &\delta_{\rm F}({\rm CDCl}_3) \ -124.7 \ ({\rm m}, \ 4-{\rm F}), \ -134.2 \ ({\rm d}, \ 8-{\rm F}), \ -137.7 \ ({\rm m}, \ 5-{\rm F}), \ -141.6 \ ({\rm q} \ {\rm of} \ {\rm d}, \ 7-{\rm F}), \ {\rm and} \\ &-146.2 {\rm ppm} \ ({\rm m}, \ 6-{\rm F}); \ \ {\rm J}_{7-{\rm F},8-{\rm F}} \ 17 \ {\rm Hz}; \ \ \delta_{\rm H}({\rm CDCl}_3) \ 6.06 {\rm ppm} \ (3-{\rm CH}); \ \ \nu_{\rm max} \ 3130 \ {\rm cm}^{-1} \\ &(3-{\rm CH}). \end{split}$$

The reaction of 4,5,6,7,8-pentafluoro-2H-cyclohepta[b]furan-2-one (9) with sodium methoxide in methanol

4,5,6,7,8-Pentafluoro-2H-cyclohepta[b]furan-2-one (9) (0.0406 g, 0.172 mmol) in anhydrous methanol (7 ml) was cooled to -70° C and treated with sodium methoxide in methanol (0.9 ml, 0.195 M; 0.175 mmol) over 4 min., the temperature rising to -67° C. The mixture was maintained at -70° for a further 10 min. after which a mixture of methanol/sulphuric acid (2 M) (1:1 v/v, 10 ml) was added. The resulting solution was extracted with ether, the extracts dried (Mg SO₄) and the solvent evaporated. The crude reaction product in CDCl₃ was examined carefully by ¹⁹F nmr. Every absorption in the spectrum was accounted for: there were six compounds present in the mixture, the major one being unreacted starting material (9) 78%. The other five compounds were the five possible -2H-cyclohepta[b]furan-2-one derivatives: 5,6,7,8-tetrafluoro-4-methoxy-2Hcyclohepta[b]furan-2-one (10), (11 parts); 4,6,7,8-tetrafluoro-5-methoxy-2Hcyclohepta[b]furan-2-one (11), (18 parts); 4,5,6,8-tetrafluoro-6-methoxy-2Hcyclohepta[b]furan-2-one (12), (8 parts); 4,5,6,8-tetrafluoro-7-methoxy-2Hcyclohepta[b]furan-2-one (12), (8 parts); 4,5,6,8-tetrafluoro-8-methoxy-2Hcyclohepta[b]furan-2-one (13), (19 parts); and 4,5,6,7-tetrafluoro-8-methoxy-2Hcyclohepta[b]furan-2-one (14), (44 parts) (see below).

The experiment described above was repeated five more times under similar conditions and once with the reactants at room temperature. The combined product from all seven experiments (1.01 g) was separated by chromatography on silica $(7" \times 2\frac{1}{2}")$ using toluene as eluant, fourteen fractions being collected; the fifteenth fraction was collected by eluting the column with ethyl acetate.

Fractions 4, 5 and 6 were combined and sublimed (0.098 g) and was a mixture of three isomeric tetrafluoro-monomethoxy-2H-cyclohepta[b]furan-2-ones (Found: C, 48.70;

H, 1.88%; M⁺, 248.
$$C_{10}H_4F_4O_3$$
 requires C, 48.40; H, 1.62%; M, 248):
4.6,7,8-tetrafluoro-5-methoxy-2H-cyclohepta[b]furan-2-one (nc) (11) (33 parts)
 $\delta_F(CDCl_3)$ -117.1 (m, 4-F), -135.0 (d, 8-F), -138.9 (m, 6-F) and -143.2ppm (q, 7-F);
J_{7-F,8-F}16 Hz; $\delta_H(CDCl_3)$ 4.02 (5-OCH₃) and 5.80ppm (3-CH);
4.5,7,8-tetrafluoro-6-methoxy-2H-cyclohepta[b]furan-2-one (nc) (12) (15 parts)
 $\delta_F(CDCl_3)$ -125.2 (m, 4-F), -131.2 (m, 5-F), -133.1 (d, 8-F) and -135.0ppm (m, 7-F);
J_{7-F,8-F}15 Hz; $\delta_H(CDCl_3)$ 3.97 (6-OCH₃) and 5.85ppm (3-CH); and
4.5,6,8-tetrafluoro-7-methoxy-2H-cyclohepta[b]furan-2-one (nc) (13) (52 parts)
 $\delta_F(CDCl_3)$ -126.3 (m, 4-F), -126.8 (s, 8-F), -136.9 (m, 5-F) and -139.5ppm (m, 6-F);
 $\delta_H(CDCl_3)$ 4.02 (7.OMe) and 5.85ppm (3-CH).

Fraction 8 contained all five possible tetrafluoro-monomethoxy-2H-cyclohepta-[b]furan-2-ones, and was particularly enriched (ca. 20%)in <u>5,6,7,8-tetrafluoro-</u> <u>4-methoxy-2H-cyclohepta[b]furan-2-one (nc) (10)</u> $\delta_{\rm F}({\rm CDCl}_3)$ -135.6 (m, 5-F), -136.0 (d, 8-F), -145.6 (m, 7-F) and -146.2ppm (m, 6-F); $\delta_{\rm H}({\rm CDCl}_3)$ early shoulder on 4.19 peak [due to (14)](4-OMe) and an early shoulder on 5.91 peak [due to(14)](3-CH).

Fractions 12 and 13 were combined (0.181 g) and shown by ¹⁹F nmr to contain the 4-methoxy compound (10) (<u>ca.</u> 2%). The major component, obtained pure by recrystallisation from toluene-light petroleum (bp. 60-80^oC) was <u>4,5,6,7-tetra-fluoro-8-methoxy-2H-cyclohepta[b]furan 2-one (nc) (14</u>), mp 76-76.5^oC. (Found: C, 48.12; H, 1.61%; M⁺, 248. C₁₀H₄F₄O₃ requires C, 48.40; H, 1.62%; M, 248) $\delta_{\rm F}$ (CDCl₃) -126.4 (m, 4-F), -134.7 (m, 7-F), -139.2 (m, 5-F), -139.2 (m, 5-F) and -146.9ppm (m, 6-F); $\delta_{\rm H}$ (CDCl₃ 4.22 (8-OCH₃) and 5.94ppm (3-CH).

Fraction 15 was sublimed at 70° C/0.05 mm Hg and after three recrystallisations from toluene-light petroleum (bp 60-80°C) followed by five recrystallisations from light petroleum (bp 60-80°C) gave a mixture of isomeric trifluoro-dimethoxy-2H-cyclohepta-[b]furan-2-ones (Found C, 50.55; H, 2.58; M⁺, 260. C₁₁H₇F₃O₄ requires C, 50.78; H, 2.71%; M, 260). The major component (74 parts) was <u>4,6,7-trifluoro-5,8-dimethoxy-2H</u> cyclohepta[b]furan-2-one (nc) (16), $\delta_{\rm F}$ (CDCl₃) -118.6 (m, 4-F), -136.2 (m, 7-F), and

-139.8ppm (m, 6–F); $\delta_{\rm H}({\rm CDCl}_3)$ 4.07 and 4.20 (unassigned 5–OMe, 8–OMe) and 5.79ppm (3–CH). The minor component(26 parts) was <u>5.6.7–trifluoro–4.8–dimethoxy–2H–cyclohepta[b]furan–2–one (nc) (15</u>), $\delta_{\rm F}({\rm CDCl}_3)$ –135.9 (m, 5–F) –138.9 (m, 7–F) and -146.4ppm (m, 6–F); $\delta_{\rm H}({\rm CDCl}_3)$ 4.12 and 4.15 (unassigned 4–OMe, 8–OMe) and 5.92ppm (3–CH).

X-ray crystallographic study of compound (14)

X-ray measurements were made using an Enraf-Nonius FAST TV area detector diffractometer and graphite monochromated Mo-K_o radiation. With a detector-to-crystal setting (= DET) of 36 mm and a swing angle (= $2\theta_{D}$) of 25⁰, reflections were found in two 5° omega rotation regions separated by 90° . Orientation matrix and unit cell dimensions were determined via the INDEX and REFINE procedures of the SADONL software (the "small molecule" online version of MADNES) using 250 reflections taken from both regions. Accurate values of DET (= 36.189 mm) and $2\theta_D$ (= 24.972) were also determined by refinement. Crystal Data: Formula: C₁₀H₄F₄O₃, M: 248.13, crystal system: monoclinic, cell dimensions: a, 16.088 (4) b, 9.154 (6) c, 13.734 (2) β , 110.669 (6) volume: 1892.42 $Å^3$, space group: I2/a, Z: 8. With a crystal of dimensions 0.2 x 0.2 x 0.3 mm, intensity data corresponding to slightly more than one hemisphere of reciprocal space were recorded using two omega scan ranges of 100° with a phi shift of 90° (to achieve > 180° in total) at chi = 0° , followed by two further omega rotations of 70° , with a phi shift of 90° at $chi = 90^{\circ}$, to record the missing cusp data. Throughout the collection the omega increment was 0.15° and the measuring time for each frame was 15s; the total data collection time was ca 18 hours. Of the reflections predicted and scanned, 13038 satisfied the conditions for acceptable measurement and were merged to give 2634 unique data points, with Rint = 0.048, of which 2004 had $F>3\sigma(F)$ and were considered observed. Data processing included corrections for Lp effects and area detector specific factors. No correction for absorption was made. The structure was solved by direct

methods. The positional and anisotropic vibrational parameters of all non-hydrogen atoms were refined anisotropically; hydrogen atoms were inserted in calculated positions, allowed to ride on the parent carbon and assigned group U_{iso} values.

Computer programs used as given in [14]. The final R and Rg values were 0.063 and 0.065 respectively with weights of $= 1/[\sigma^2(F) + 0.001134F_0^2]$ giving flat agreement analyses. Final atomic coordinates of non-H atoms are given in Table 1 and important bond lengths and angles are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H atom coordinates, thermal parameters and remaining bond lengths and angles.

The structure of compound (14), determined by this study, is shown in Figure 1. There is no obvious explanation why the bond lengths C(2)-O(1) and C(10)-O(1) are not more nearly the same.



Fig. 1. Structure of compound (14).

	x	У	Z	
O(1)	4908(1)	644(1)	7931(1)	
O(2)	6028(1)	1442(2)	7433(1)	
O(3)	3338(1)	$382(2)^{2}$	8205(1)	
F(1)	6616(1)	-2903(1)	10020(1)	
F(2)	5573(1)	-4017(1)	10844(1)	
F(3)	3965(1)	-3513(2)	10470(1)	
F(4)	2969(1)	-1618(2)	9281(1)	
C(1)	5623(1)	-1225(2)	8974(1)	
C(2)	4797(1)	-432(2)	8555(1)	
C(3)	4003(1)	-570(2)	8676(1)	
C(4)	3805(1)	-1638(2)	9317(2)	
C(5)	4333(2)	-2655(2)	9950(2)	
C(6)	5234(2)	-2970(2)	10135(2)	
C(7)	5787(1)	-2378(2)	9705(1)	
C(9)	6214(2)	-614(2)'	8596(2)	
C(10)	5792(2)	$572(2)^{-1}$	7932(2)	
C(8)	2895(2)	210(4)	7110(2)	

Fractional Co-ordinates ($\times 10^4$) for $C_{10}H_4F_4O_3$.

TABLE 2

Bond lengths and angles for $\mathrm{C}_{10}\mathrm{H}_4\mathrm{F}_4\mathrm{O}_3$

a) bond lengths (Å)							
$\begin{array}{c} C(2)-O(1)\\ C(10)-O(2)\\ C(8)-O(3)\\ C(6)-F(2)\\ C(4)-F(4)\\ C(7)-C(1)\\ C(3)-C(2)\\ C(5)-C(4)\\ C(7)-C(6) \end{array}$	$\begin{array}{c} 1.358(3)\\ 1.197(3)\\ 1.427(3)\\ 1.338(3)\\ 1.327(3)\\ 1.415(3)\\ 1.350(3)\\ 1.350(3)\\ 1.350(3)\\ 1.344(3) \end{array}$	$\begin{array}{c} C(10)-O(1)\\ C(3)-O(3)\\ C(7)-F(1)\\ C(5)-F(3)\\ C(2)-C(1)\\ C(9)-C(1)\\ C(4)-C(3)\\ C(6)-C(5)\\ C(10)-C(9) \end{array}$	$\begin{array}{c} 1.422(3)\\ 1.355(3)\\ 1.337(3)\\ 1.332(3)\\ 1.444(3)\\ 1.355(3)\\ 1.426(3)\\ 1.411(3)\\ 1.427(3) \end{array}$				
b) bond angles (d C(10)-O(1)-C(2) C(7)-C(1)-C(2) C(9)-C(1)-C(7) C(3)-C(2)-O(1) C(2)-C(3)-O(3) C(4)-C(3)-C(2) C(5)-C(4)-F(4) C(4)-C(5)-F(3) C(6)-C(5)-C(4) C(7)-C(6)-F(2) C(1)-C(7)-F(1) C(6)-C(7)-C(1) O(2)-C(10)-O(1) C(9)-C(10)-O(2)	eg))	$\begin{array}{c} 108.7(2)\\ 125.0(2)\\ 126.8(3)\\ 119.1(2)\\ 120.3(2)\\ 124.6(2)\\ 115.6(2)\\ 117.0(3)\\ 129.1(2)\\ 116.5(3)\\ 114.4(2)\\ 128.7(3)\\ 119.2(3)\\ 134.1(2) \end{array}$	$\begin{array}{c} C(8)-O(3)-C(3)\\ C(9)-C(1)-C(2)\\ C(1)-C(2)-O(1)\\ C(3)-C(2)-C(1)\\ C(4)-C(3)-O(3)\\ C(3)-C(4)-F(4)\\ C(5)-C(4)-F(3)\\ C(6)-C(5)-F(3)\\ C(6)-C(5)-F(3)\\ C(5)-C(6)-F(2)\\ C(7)-C(6)-C(5)\\ C(6)-C(7)-F(1)\\ C(10)-C(9)-C(1)\\ C(9)-C(10)-O(1)\\ \end{array}$	$\begin{array}{c} 116.6(2)\\ 108.1(2)\\ 108.0(2)\\ 132.9(1)\\ 115.1(2)\\ 114.4(2)\\ 130.0(3)\\ 114.0(2)\\ 113.9(2)\\ 129.5(2)\\ 116.8(2)\\ 108.6(3)\\ 106.6(2)\\ \end{array}$			

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