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Synthesis, variable temperature NMR investigations and solid state characterization of novel octafluorofluorene compounds

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ABSTRACT

The preparation of a number of new 9-substituted octafluorofluorene derivatives, solution NMR studies, and the first examples of solid state structures of octafluorofluorenes [1,2,3,4,5,6,7,8-octafluorofluorene, $C_{13}H_2F_8$, **1**; 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluoro)phenylfluorene, $C_{19}HF_{13}$, **8**; 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,7,7′,8,8′-hexadecafluoro-9,9′-bifluorenyl, $C_{26}H_2F_{16}$, **11**] are reported. Variable temperature ^{19}F NMR investigations have been performed on the 9-aryl substituted compounds 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluoro)phenyl-9-hydroxyfluorene, $C_{19}HF_{13}O$, **4**, 1,2,3,4,5,6,7,8-octafluoro-9-(nonafluoro-4′-biphenylyl)-9-hydroxyfluorene, $C_{25}HF_{17}O$, **5**, and **8**, and the energetic barriers to rotation of the aryl have been determined. A lower rotational barrier is observed for compound **4** with respect to compound **8**, while **5** does not show fluxional behaviour below 338 K. The results of the variable temperature experiments performed on **8** have been rationalized by 2D NMR studies, and compared to the solid state data resulting from the X-ray structural analysis.

1. Introduction

The fluorination of aryl groups determines important effects in reactivity [1]. More specifically, fluoro- and polyfluoro aryl substituents can induce stabilizing effects on carbanions, when compared with the analogous all-hydrogen systems [2]. This stabilization has been observed in tetraarylborate ions: for instance, the tetraphenylborate $[B(C_6H_5)_4]^-$ is thermally unstable and decomposes under acidic and oxidant conditions [3], while the 3,5-fluoroalkyl-substituted anions $\{B[C_6H_3(R_f)_2]_4\}^-$ [$R_f = CF_3$, $(CF_2)_3CF_3$, $CF(CF_3)_2$] are thermally stable and resist highly acidic conditions [4]. Relevantly, when used in olefin polymerization, the salts of these fluorine-rich anions are better co-catalysts than the non-fluorinated ones [5].

Fluoro-substituted fluorene derivatives have been known for a long time [6], and some of these compounds have attracted interest for their biological properties [7] or for their possible use as standards in environmental analyses [8].

Within the series of fluoro-substituted fluorenes, a limited number of octafluorofluorene species have been reported [1c,2,9]. Some of us have recently described the catalytic properties of octafluorofluorenyl anions [10], which made us keen on the preparation of new octafluorofluorene compounds. The synthetic procedures are reported herein, together with the spectroscopic characterization (^1H and ^{19}F NMR), and some X-ray molecular determinations; furthermore, variable temperature ^{19}F NMR experiments will be discussed.

2. Results and discussion

2.1. Synthesis

Some of the octafluorofluorene derivatives discussed in this paper [1,2,3,4,5,6,7,8-octafluorofluorene, $C_{13}H_2F_8$, **1**; 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluoro)phenylfluorene, $C_{19}HF_{13}$, **8**; 1,2,3,4,5,6,7,8-octafluoro-9-hydroxyfluorene, $C_{13}H_2F_8O$, **9**] have been prepared according to the literature [2,9] while new high-yield synthetic procedures have been developed for the derivatives **2–7, 10–11**. Compounds **2–5** (9-aryl substituted octafluoro-9-hydroxyfluorenes) have been obtained by reaction of octafluorofluorenone with

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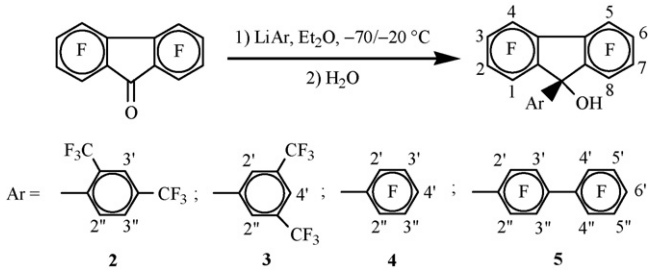
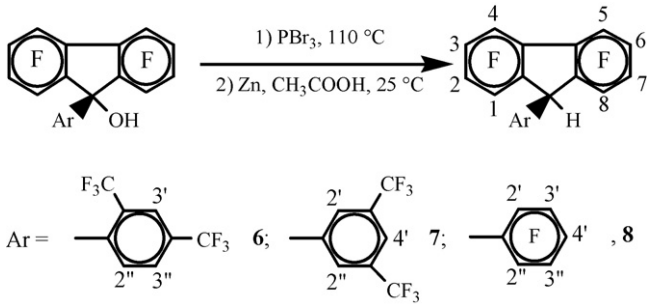


Scheme 1.



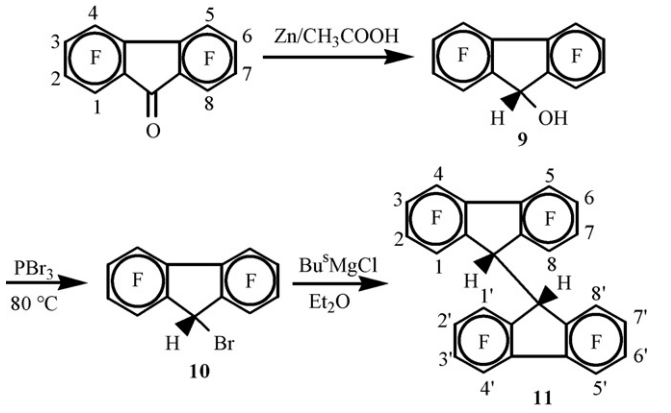
Scheme 2.

one equivalent of LiAr [Ar = 2,4-bis(trifluoromethyl)phenyl, 3,5-bis(trifluoromethyl)phenyl, (pentafluoro)phenyl, (nonafluoro)-4-biphenylyl], in diethyl ether at temperatures in the range between −70 and −20 °C, see Scheme 1.

The octafluorofluorenes, **6**–**8**, have been obtained from the hydroxo derivatives, **2**–**4**, by bromination with PBr_3 followed by reduction with zinc in acetic acid at room temperature (Scheme 2). Dimer **11** was obtained from 1,2,3,4,5,6,7,8-octafluorofluorenone by the sequence of reactions illustrated in Scheme 3. Compounds **2**–**11** are colourless crystalline materials, and have been characterized by ^1H and ^{19}F NMR spectroscopy. Moreover, the solid state molecular structures of **1**, **8** and **11** have been ascertained by X-ray diffraction analyses.

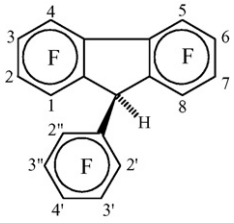
2.2. NMR studies

The ^1H NMR spectra of compounds **6**–**11** (in $CDCl_3$) show the presence of a relatively low-field resonance, due to the C(sp^3)-*H* proton, in the range 5.40 (**11**)–6.16 (**9**) ppm, as consequence of the electron withdrawing action of the octafluorofluorenyl frame. Otherwise, the ^1H NMR spectra ($CDCl_3$) of **2**–**5**, **9** exhibit the peak assigned to the O*H* proton in the range 2.62 (**9**)–3.75 (**4**) ppm.



Scheme 3.

Table 1
^{19}F NMR resonances of **8** in various solvents.



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	CCl_4[a]	C_6D_6	THF	$CDCl_3$
1, 8	−143.3	−144.3	−131.3	−152.1
3, 6	−153.9	−153.7	−150.8	−152.4
4, 5	−134.7	−134.4	−140.0	−143.1
2′(2″)	−142.1	−142.6	−139.0	−142.6
2″	~	−143.6	−138.5	−141.6
3′(3″)	−161.5	−160.7	−158.3	−160.7
3″	~	~	−157.9	−160.1
4′	−153.9	−152.0	−150.5	−152.4

[a] δ-Values referred to $CFCl_3$, recalculated from ref [9a].

In the ^{19}F NMR spectra, the fluorine atoms belonging to the fluorenyl unit resonate respectively at *ca.*−130 ppm (F1, F8), −140 ppm (F4, F5) and −150 ppm (F2, F7, F3, F6).

We noticed that the ^{19}F NMR spectrum of **8** in THF-d^8 appeared markedly different from that reported by Vlasov (recorded in CCl_4) [9a], then we decided to deepen this point. The solution structure of **8** has been elucidated by means of 1D and 2D ^{19}F NMR experiments: at 298 K, the monodimensional spectrum in THF-d^8 shows four resonances for the fluorenyl moiety, indicating the equivalence of the two C_6-rings. On the other hand, the presence of five signals for the C_6F_5 group suggests that both the *ortho*- and the *meta*-positions on the (pentafluoro)phenyl ring are non-equivalent. The ^{19}F,^{19}F-COSY and NOESY spectra have led to the assignments reported in Table 1.

Interestingly the ^{19}F,^{19}F-NOESY spectrum of **8** only shows correlation between the fluorines F1/F8 and F2′, while no cross-peak is observed between F1/F8 and F2″. According to this, the orientation of the pentafluorophenyl with respect to the fluorenyl moiety should be non-symmetric, making both the *ortho*- and *meta*-positions at the aryl ring non-equivalent. However, exchange cross-peaks have been observed both between F2′ (−139.0 ppm) and F2″ (−138.5 ppm), and between F3′ (−158.3 ppm) and F3″ (−157.9 ppm): these features suggest that, although the aryl rotation is slow at room temperature, it is not completely inhibited.

Hence, a variable temperature ^{19}F NMR study was carried out on compound **8** in THF-d^8 (see Fig. 1) and, for comparison, in $CDCl_3$, too. As a general remark, the hindered rotation of the aryl ring is observable both in THF-d^8 and in $CDCl_3$. Nevertheless, the coalescences of the resonances due to the non-equivalent F2′ and F2″, and F3′ and F3″, respectively, have been seen at different temperatures on varying the solvent (see Table 2).

The rate constants, k_c, and the activation free energy, $\Delta G^{\#}$, for the C_6F_5 ring rotation, have been calculated according to the equations: $k_c = \pi\left(\Delta\delta/\sqrt{2}\right)$ ($\Delta\delta$ is the difference between the chemical shifts of the two resonances related to either the *o*-fluorines or the *m*-fluorines respectively) and $\Delta G = 4.57T_c(10.32 + \ln(T_c/k_c))$, where T_c is the coalescence temperature (K), see Table 2 [11].

The ^{19}F NMR spectrum of **4**, which differs from **8** for the presence of the hydroxy-substituent (see Schemes 1 and 2), exhibits only one narrow doublet for the fluorine nuclei F2′ and F2″ (the multiplicity is consequence of the coupling with F3′/F3″) and one multiplet for the fluorines F3′ and F3″ (due to the couplings with F2′/F2″ and F4′), in THF-d^8 at room temperature. These

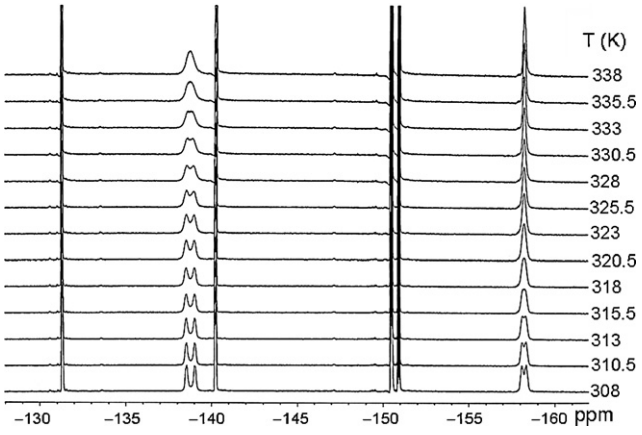


Fig. 1. Variable temperature ^{19}F NMR study on compound **8** (solvent: THF-d^8).

features indicate that the rotation of the pentafluorophenyl substituent in **4** occurs rapidly on the NMR timescale already at room temperature. As the temperature is lowered, the doublet observed at room temperature for F2′/F2″ gradually broadens and splits into a pair of doublets below 222 K (T_{cF2}). Analogously, the F3′/F3″ resonance, which appears as a multiplet at room temperature, splits into two false-triplets below 245 K. A similar behaviour has been observed in $CDCl_3$ (see Table 2 for T_c). The activation parameters calculated from these observations for compound **4** are reported in Table 2; the chemical shift separation in the absence of exchange has been estimated on the lowest temperature (208 K) spectra (THF-d$_8$: 0.28 ppm for F2′/F2″ and 2.01 ppm for F3′/F3″; $CDCl_3$: 0.30 ppm for F2′/F2″ and 2.01 ppm for F3′/F3″). It is noteworthy that the *o*-fluorines within the aryl substituent (F2′, F2″) resonate at significantly different chemical shifts in compound **4** (−135.9 ppm) with respect to **8** (−138.5 and −139.0 ppm), at 298 K in THF-d^8. This discrepancy might be the effect of a hydrogen-bond involving the adjacent hydroxyl group in **4**. However, an interaction F···H–O, if present [12], is evidently not strong enough to prevent the fast rotation of the aryl ring at room temperature.

The ^{19}F NMR spectrum of compound **5** (see Scheme 1) in THF-d^8, exhibits three pairs of distinct resonances for the fluorines F2′ and F2″, F3′ and F3″, F4′ and F4″, respectively. Such resonances are observed at −131.9 and −132.7 ppm, −148.9 and −150.7 ppm, −134.2 and −134.4 ppm, in the order given. On increasing the temperature up to 338 K (the highest temperature we could reach in THF-d^8), the spectrum remains substantially unchanged, suggesting that the rotational barrier around the C(sp^3)-Ar bond is much higher for compound **5** than for **4** and **8**. This result appears to be an effect of the higher moment of inertia of the nonafluorobiphenylyl substituent, compared with that of the pentafluorophenyl substituent, see Schemes 1 and 2. According to that, the energy needed to overcome the rotational barrier increases significantly on passing from **4**, **8** to **5**, with consequent rise of the coalescence temperature.

The higher rotational barrier of the $-C_6F_5$ unit observed in **8** with respect to **4** (see Table 2) is coherent with previous results found for 9-substituted-9-arylfluorenes [9]. In agreement with these reports, the activation free energy for the rotation of the aryl would depend on the encumbrance of the R substituent (R=H, OH): the larger R is, the higher is the energetic level of the ground state, and the smaller is the energy difference between the ground state and the transition one.

In addition, the observed little barriers (10–15 kcal/mol) and the negligible influence of the solvent (THF-d$_8$ *vs.* $CDCl_3$) suggest that the aryl rotation takes place *via* a non-dissociative mechanism, ruling out the dissociative mechanistic proposal formulated by Chandross and Sheley for related substituted fluorenes [13].

Table 2
Spectral, kinetic and activation parameters related to the rotation of the pentafluorophenyl ring in compounds **4** and **8**.

	$\Delta\delta$ (Hz)		k_c (s^{-1})		T_c (K)		$\Delta G^{\#}$ (kcal mol^{-1})
	F2′/F2″	F3′/F3″	F2′/F2″	F3′/F3″	F2′/F2″	F3′/F3″	
THF-d^8							
4	78 ± 3	567 ± 4	175 ± 7	1259 ± 9	222	245	10.2 ± 0.5
8	134 ± 3	71 ± 6	310 ± 22	158 ± 13	333	316	15.8 ± 0.1
$CDCl_3$							
4	1881 ± 3	242 ± 4	4176 ± 7	537 ± 9	265	245	9.9 ± 0.7
8	310 ± 3	132 ± 3	688 ± 7	293 ± 7	343	329	15.4 ± 0.3

2.3. X-ray structural studies of 1, 8, and 11

A search on the Cambridge Crystallographic Data Centre [14] revealed the absence of crystallographically characterized octafluoro-substituted fluorenes. This fact prompted us to investigate the X-ray molecular structure of some of the compounds reported in the previous section, with particular regard to **8** (we were eager to see whether the features evidenced in solution by ^{19}F NMR spectroscopy found correspondence in the solid state or not).

Crystals suitable for X-ray analyses were collected by slow evaporation of the solvents from toluene (compounds **8** and **11**) or C_6D_6 (compound **1**) solutions. The species **1** and **8** crystallize in the monoclinic space group *C*2/*c*. Figs. 2 and 3 show the molecular

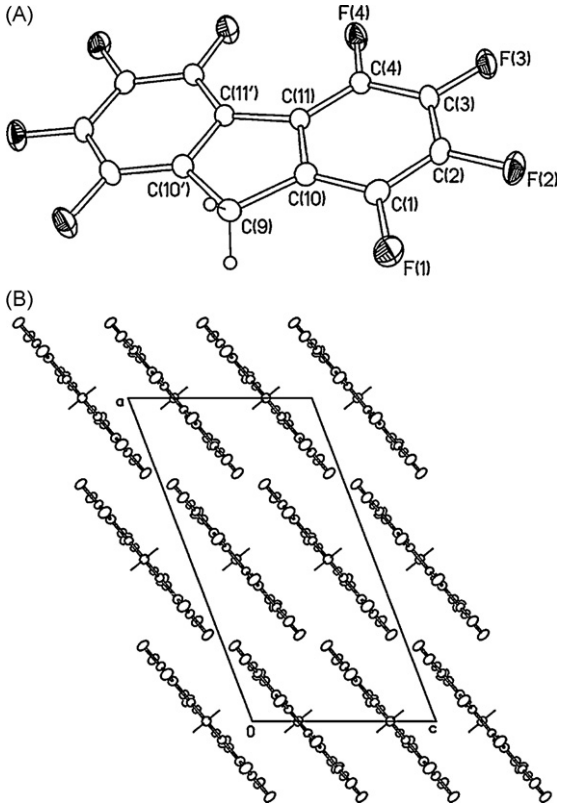


Fig. 2. View of the molecular structure (A) and of the crystal packing along the axis **b** (B) of 1,2,3,4,5,6,7,8-octafluorofluorene, **1**. Thermal ellipsoids are drawn at 30% probability level.

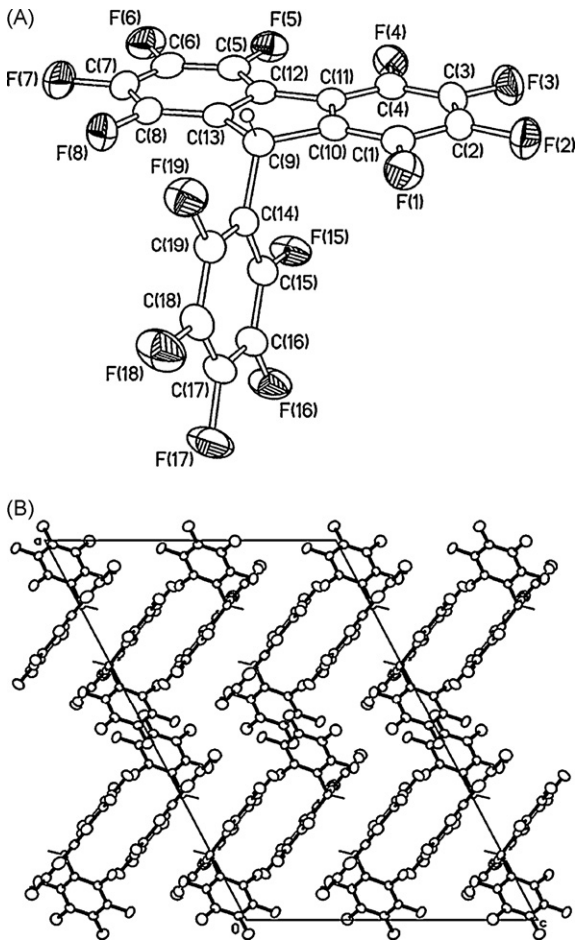


Fig. 3. View of the molecular structure (A) and of the crystal packing along the axis **b** (B) of 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluorophenyl)fluorene, **8**. Thermal ellipsoids are drawn at 30% probability level.

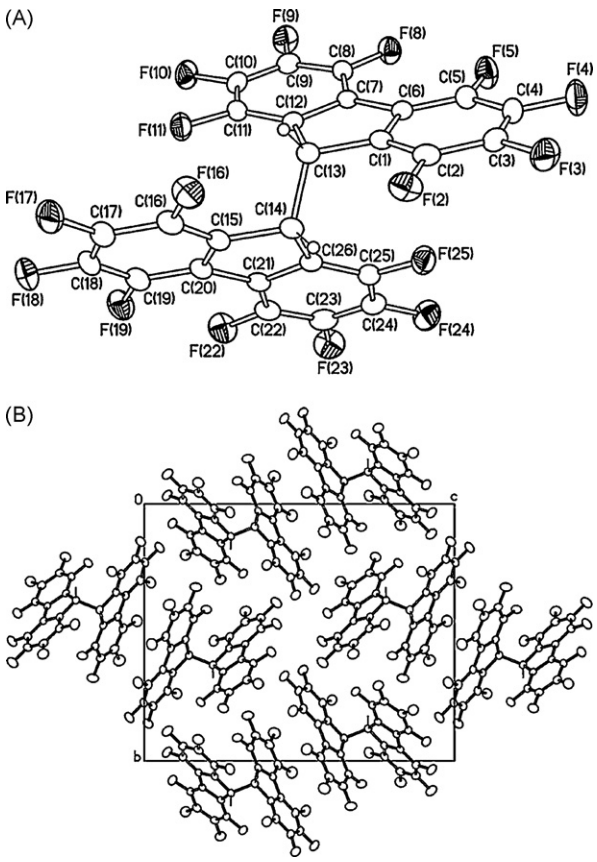


Fig. 4. View of the molecular structure (A) and of the crystal packing along the axis **b** (B) of 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,7,7′,8,8′-hexadecafluoro-9,9′-bifluorenyl, **11**. Thermal ellipsoids are drawn at 30% probability level.

structures and the crystal packing of the two compounds. Bond distances and angles for **1** and **8** are given as Supporting Information.

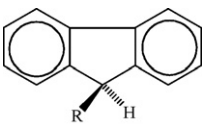
Compound **1** (Fig. 2A) possesses a twofold symmetry and is essentially planar, the maximum deviation (0.03 Å) occurring at F(4). As shown in Fig. 2B, the molecules align along the (1 0 1) plane.

For what concerns **8**, Fig. 3A, the molecules are arranged in infinite columns parallel to axis **b**, the octafluorofluorenyl moieties being approximately aligned with the plane (3 0 $\bar{7}$), Fig. 3B. By a different point of view, the same molecules are distributed along two planes: one of them is defined by the octafluorofluorenyl frames, the maximum deviation being 0.08 Å at F(7), while the second plane is defined by the pentafluorophenyl rings [max deviation 0.02 Å at F(17)]. Noteworthy, the two planes form a dihedral angle of 83.5°, resembling the non-equivalence of the *ortho*- and *meta*-positions within the aryl ring, which is observed also in solution even at room temperature (see above). A molecular layout analogous to that found for **8** is regularly exhibited by species containing the 9-aryl-fluorene unit [15], the dihedral angle between the aryl and the fluorine units ranging between 72.9° and 89.1°.

The molecular structure of **11** is shown in Fig. 4A, whereas bond distances and angles are provided as Supporting Information. The structure of the two equivalent fluorenyl moieties is similar to that observed in non-fluorinated 9,9′-bifluorenyl [16] and in 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,7,7′,8,8′-hexadecachloro-9,9′-bifluorenyl [17]. Likewise these compounds, **11** shows a *gauche* conformation, and only slight differences in the torsion angle C(1)C(13)C(14)C(26) are displayed in the three cases: the value of this angle is 61.9° in 9,9′-bifluorenyl [16], 67.6° and 74.4° in the two independent molecules of 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,7,7′,8,8′-hexadecachloro-9,9′-bifluorenyl [17] and 72.5° in **11**.

As a general consideration, the X-ray structures of **1**, **8**, and **11** display similar average C–C bond distances, within the aryl rings, which resemble the corresponding values observed in the ions $[B(C_6F_5)_4]^-$ [18] and $[BH(C_6F_5)_3]^-$ [19]. The C(sp^3)–C distances, Table 3, do not vary significantly on going from phenyl [20] (or *p*-tolyl- [21]) substituted fluorenes to **8**. The increase of the C(sp^3)–C distances on going from the 9-aryl- to the 9-fluorenyl substituted species is due to fact that both these carbon atoms are sp^3-hybridized in the latter. Moreover, the C(sp^2)–F lengths appear comparable to those found in perfluorinated organic molecules [22].

Table 3
C(sp^3)–C(*R*) distances (Å) in selected 9-substituted fluorenes.



R	C(sp^3)–C(*R*) distance (Å)	Reference
C_6H_5	1.523(6)	[20]
p-$CH_3C_6H_4$	1.515(7)	[21]
C_6F_5	1.521(4)	This work
$C_{13}H_9$	1.542(5); 1.539(6)	[16a,d]
$C_{13}HF_8$	1.577(3)	This work

3. Conclusions

Some novel octafluorofluorene derivatives have been described here for the first time as prepared in high yields by standard routes.

Variable temperature ^{19}F NMR solution studies performed on octafluoro-9-arylfluorenes have allowed to estimate kinetic parameters related to the aryl ring rotational motion. According to these studies, the substitution of one hydrogen with one hydroxyl group at the quaternary carbon makes the rotation of the aryl moiety around the C(sp^3)–aryl bond more rapid, in agreement with previous reports regarding analogous non-fluorinated systems. Moreover, variable temperature NMR experiments carried out in solvents of different polarities have ruled out the possibility that a dissociative mechanism is involved in the aryl rotational process.

The X-ray solid state structures determined for 1,2,3,4,5,6,7,8-octafluorofluorene, 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluorophenyl)fluorene, and 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,-7,7′,8,8′-hexadecafluoro-9,9′-bifluorenyl represent the first crystallographic reports concerning octafluorofluorene compounds. Comparisons of the structural features with those available for all-hydrogen analogous molecules have pointed out that the substitution with fluorine atoms does not determine dramatic changes in the geometry and in the crystal packing.

4. Experimental

4.1. General

Unless otherwise stated, all the operations were carried out under atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. ^1H and ^{19}F NMR spectra at 298 K were recorded on Varian Gemini 200BB instrument (200 MHz for ^1H and 188 MHz for ^{19}F), while variable temperature ^{19}F NMR spectra were recorded on Varian VXR 300 (282 MHz for ^{19}F). TMS and $CFCl_3$ were used as standard for ^1H NMR and ^{19}F NMR spectra, respectively. The compounds 1,2,3,4,5,6,7,8-octafluorofluorene, **1** [1c], 1,2,3,4,5,6,7,8-octafluorofluorenone [23], and 4-Br-nonafluoro-1,1′-biphenyl [24] were prepared according to literature procedures.

4.2. Preparation of 1,2,3,4,5,6,7,8-octafluoro-9-hydroxy-9-arylfluorene derivatives, 2–5

Only the preparation of 1,2,3,4,5,6,7,8-octafluoro-9-hydroxy-9-[2,4-bis(trifluoromethyl) phenyl]fluorene, **2**, is described in detail, those of compounds **3**–**5** being performed in a similar way. A solution of 1-bromo-2,4-bis(trifluoromethyl)benzene (5.00 g, 17.1 mmol), in diethyl ether (100 ml), was added to a 2.5 M solution of butyl-lithium in diethyl ether (7.00 mL; 17.5 mmol of butyl-lithium), at *ca.* −75 °C. After 1 h stirring at this temperature, 1,2,3,4,5,6,7,8-octafluorofluorenone (6.00 g, 17.84 mmol) was added. The mixture was additionally stirred for 1 h and then hydrolyzed with water. The resulting two phases were separated, then the aqueous liquor was washed with diethyl ether (2 × 50 mL). The ether solutions were unified and dried over Na_2SO_4. The solvent was evaporated to dryness and the residue was treated with cold petroleum ether. The solution obtained was filtered and then dried *in vacuo*, so obtaining 2.55 g (56% yield) of **2** as colourless crystalline solid. Anal. Calcd. for $C_{21}H_4F_{14}O$: C, 46.86, H, 0.75. Found C, 46.91, H, 0.71%. ^1H NMR ($CDCl_3$): δ 8.80 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, H3″); 8.00 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, H2″); 7.90 (s, 1 H, H3′); 3.00 (s, 1 H, OH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 1 for the fluorine atoms numbering): δ −63.2, −58.2 (br, 6 F, CF_3), −133.3 (d, $^3J_{FF}$ = 19.5 Hz, 2 F, F1 + F8), −143.3 (d, $^3J_{FF}$ = 19 Hz, 2 F, F4 + F5), −150.2 (m, 2 F, F2 + F7), −152.0 (m, 2 F, F3 + F6).

1,2,3,4,5,6,7,8-Octafluoro-9-hydroxy-9-(3,5-trifluoromethylphenyl)fluorene, **3**: Colourless microcrystalline solid, 95% yield from 3,5-bis(trifluoromethyl)phenyllithium, freshly prepared from 1-bromo-3,5-bis(trifluoromethyl)benzene, and 1,2,3,4,5,6,7,8-octafluorofluorenone, after purification on a silica gel column [eluent: petroleum ether/acetone = 90/10 (*v*/*v*)]. Anal. Calcd. for $C_{21}H_4F_{14}O$: C, 46.86; H, 0.75. Found C 46.69; H, 0.78%. ^1H NMR ($CDCl_3$): δ 7.87 (s, 1 H, H4′); 7.84 (s, 2 H, H2′ + H2″); 3.20 (s, 1 H, OH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 1 for the fluorine atoms numbering): δ −62.9 (s, 6 F, CF_3), −132.6 (d, $^3J_{FF}$ = 20.0 Hz, 2 F, F1 + F8), −142.1 (d, $^3J_{FF}$ = 19.8 Hz, 2 F, F4 + F5), −149.3 (m, 2 F, F2 + F7), −150.5 (m, 2 F, F3 + F6) ppm.

1,2,3,4,5,6,7,8-Octafluoro-9-hydroxy-9-pentafluorophenylfluorene, **4**: Colourless microcrystalline solid, 93% yield from pentafluorophenyl lithium, freshly prepared from 1-bromo-pentafluorobenzene, and 1,2,3,4,5,6,7,8-octafluorofluorenone. Anal. Calcd. for $C_{19}HF_{13}O$: C, 46.36; H, 0.20. Found: C, 46.31; H, 0.22%. ^1H NMR ($CDCl_3$): δ 3.75 (s, 1 H, OH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 1 for the fluorine atoms numbering): δ −133.0 (d, $^3J_{FF}$ = 19.5 Hz, 2 F, F1 + F8), −141.0 (d, $^3J_{FF}$ = 19.3 Hz, 2 F, F2′ + F2″), −143.8 (d, $^3J_{FF}$ = 19.5 Hz, 2 F, F4 + F5), −149.7 (m, 2 F, F2 + F7); −151.4 (m, 2 F, F3 + F6), −151.7 (t, $^3J_{FF}$ = 21.1 Hz, 1 F, F4′), −159.8 (m, 2 F, F3′ + F3″) ppm. ^{19}F NMR (THF-d^8, see Scheme 1 for the fluorine atoms numbering): δ −131.3 (d, $^3J_{FF}$ = 19.8 Hz, 2 F, F1 + F8), −135.9 (d, $^3J_{FF}$ = 19.3 Hz, 2 F, 2 F, F2′ + F2″), −140.2 (d, $^3J_{FF}$ = 19.5 Hz, 2 F, F4 + F5), −149.3 (m, 2 F, F2 + F7), −150.0 (m, 2 F, F3 + F6), −151.4 (t, $^3J_{FF}$ = 21.2 Hz, 1 F, F4′), −159.0 (m, 2 F, F3′ + F3″) ppm.

1,2,3,4,5,6,7, 8-Octafluoro-9-hydroxy-9-nonafluorodiphenylfluorene, **5**: Colourless microcrystalline solid, 96% yield from (nonafluoro)-4-biphenylyl lithium, freshly prepared from 4-bromo(nonafluoro)-4-biphenylyl, and 1,2,3,4,5,6,7,8-octafluorofluorenone, after purification on a silica gel column [eluent: petroleum ether/acetone 90/10 (*v*/*v*)]. Anal. Calcd. for $C_{25}HF_{17}O$: C, 46.90; H, 0.16. Found: C, 46.81; H, 0.13%. ^1H NMR ($CDCl_3$): δ 3.35 (s, 1 H, OH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 1 for the fluorine atoms numbering): δ −133.0 (m, 2 F, F1 + F8), −133.6 (d, $^3J_{FF}$ = 21.5 Hz, 1 F, F2′), −136.3 (d, $^3J_{FF}$ = 21.5 Hz, 1 F, F2″), −137.9 (d, $^3J_{FF}$ = 19.8 Hz, 1 F, F4′), −138.3 (d, $^3J_{FF}$ = 19.5 Hz, 1 F, F4″), −141.7 (m, 2 F, F4 + F5), −149.9 (m, 2 F, F2 + F7), −151.4 (m, 3 F, F3, F6 + F6'), −152.6 (d, $^3J_{FF}$ = 20.0 Hz, 1 F, F3′), −153.9 (d, $^3J_{FF}$ = 19.7 Hz, 1 F, F3″), −163.3 (m, 2 F, F5′ + F5″) ppm. ^{19}F NMR (THF-d^8, see Scheme 1 for the fluorine atom numbering): δ −131.0 (m, 2 F, F1 + F8), −131.9 (d, $^3J_{FF}$ = 21.1 Hz, 1 F, F2), −132.7 (d, $^3J_{FF}$ = 21.0 Hz, 1 F, F2″), −134.2 (d, $^3J_{FF}$ = 21.0 Hz, 1 F, F4′), −134.4 (d, $^3J_{FF}$ = 21.1 Hz, 1 F, F4″), −138.5 (m, 2 F, F4 + F5), −148.6 (m, 2 F, F2 + F7), −149.6 (m, 2 F, F3 + F6), −151.9 (t, $^3J_{FF}$ = 21.0 Hz, 1 F, F6′), −148.9 (d, $^3J_{FF}$ = 21.0 Hz, 1 F, F3′), −150.7 (d, $^3J_{FF}$ = 19.6 Hz, 1 F, F3″), −161.2 (m, 2 F, F5′ + F5″) ppm.

4.3. Preparation of 1,2,3,4,5,6,7,8-octafluoro-9-arylfluorene derivatives, 6–8

Only the preparation of 1,2,3,4,5,6,7,8-octafluoro-9-[2,4-bis(trifluoromethyl)phenyl]fluorene, **6**, is described in detail, those of compounds **7**–**8** being performed in a similar way. A mixture of **2** (0.950 g, 1.85 mmol) and PBr_3 (10.0 mL, 0.106 mol) was heated at 110–120 °C for 40 min (30 min in the case of **8**). Hence, the reaction mixture was hydrolysed on ice, and washed with diethylether (3 × 40 mL). The combined ethereal extracts were washed with a 10% aqueous solution of $NaHCO_3$, and then were dried over Na_2SO_4, filtered and finally dried *in vacuo*. The residue so obtained was dissolved in 20 mL of acetic acid, and treated with zinc (1.05 g, 16.1 mmol). The resulting mixture was stirred for 1 h at 25 °C, hydrolyzed in water, and then washed with diethyl ether (2 × 30 mL). The ethereal extracts were unified, and washed with a 10% aqueous solution of $NaHCO_3$. Afterwards, the ethereal solution

was dried over Na_2SO_4, filtered and dried *in vacuo*. The raw material was purified by chromatography on a silica gel column using petroleum ether as eluent. Compound **6** was obtained as a colourless crystalline material upon removal of the solvent (0.61 g, 72% yield). Anal Calcd. for $C_{21}H_4F_{14}$: C, 48.30, H, 0.77. Found C, 48.36, H, 0.80%. ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 1 H, H3′); 7.60 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, H2″); 6.70 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, H3″); 5.86 (s-br, 1 H, CH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 2 for the fluorine atoms numbering): δ −58.3, −63.2 (s, 6 F, CF_3); −133.9 (d, $^3J_{FF}$ = 20 Hz, 2 F, F1 + F8), −140.9 (d, $^3J_{FF}$ = 19.5 Hz, 2 F, F4 + F5), −152.3 (m, 4 F, F2 + F7 + F3 + F6) ppm.

1,2,3,4,5,6,7,8-Octafluoro-9-(3,5-trifluoromethylphenyl)fluorene, **7**: Colourless microcrystalline solid, 77% yield from **3**. Anal. Calcd. for $C_{21}H_4F_{14}$: C, 48.30, H, 0.77. Found C, 48.40, H, 0.81%. ^{1}H NMR ($CDCl_3$): δ 7.84 (s, 1 H, H4′); 7.53 (s, 2 H, H2′ + H2″); 5.57 (s-br, 1 H, CH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 2 for the fluorine atoms numbering): δ −63.0 (s, 6 F, CF_3); −133.5 (d, $^3J_{FF}$ = 19 Hz, 2 F, F1 + F8); −141.2 (d, $^3J_{FF}$ = 19.8 Hz, 2 F, F4 + F5); −151.9 (m, 2 F, F2 + F7); −152.2 (m, 2 F, F3 + F6) ppm.

1,2,3,4,5,6,7,8-Octafluoro-9-(pentafluorophenyl)fluorene, **8**: Colourless microcrystalline solid, 84% yield from **4**, after chromatography on silica gel [eluent: petroleum ether/CH_2Cl_2 98/2 (*v*/*v*)]. Anal. Calcd. for $C_{19}HF_{13}$: C, 47.92; H, 0.21. Found: C, 47.81; H, 0.19%. ^{1}H NMR ($CDCl_3$): δ 5.78 (s-br, 1 H, CH) ppm. ^{19}F NMR: see Table 1 for the assignment of the fluorine resonances and Scheme 2 for the fluorine atoms numbering.

4.4. Preparation of 9-hydroxy-9H-octafluorofluorene, 9

A suspension of 1,2,3,4,5,6,7,8-octafluorofluorenone (2.03 g, 6.26 mmol), in acetic acid (20 mL), was treated with finely divided zinc (0.998 g, 15.3 mmol). The mixture was stirred at room temperature for 1 h, then a TLC analysis [eluent: petroleum ether/acetone 8/2 (*v*/*v*)] revealed that complete consumption of starting fluorenone had occurred. Subsequently, water (150 mL) was added to the mixture, then the resulting mixture was treated with diethyl ether (3 × 50 mL). The solvent was removed from the extracted ethereal materials, thus colourless crystalline compound **9** (1.88 g, 92% yield) was obtained. Anal. Calcd. for $C_{13}H_2F_8O$: C, 47.87, H, 0.62. Found C, 47.73, H, 0.63%. ^{1}H NMR ($CDCl_3$): δ 6.16 (s, 1 H, CH), 2.62 (s, 1 H, OH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 3 for the fluorine atoms numbering): δ −134.3 (m, 2 F, F1 + F8); −142.5 (d, $^3J_{FF}$ = 19.3 Hz, 2 F, F4 + F5); −151.3 (m, 2 F, F2 + F7); −152.8 (m, 2 F, F3 + F6) ppm.

4.5. Preparation of 9-Br-9H-octafluorofluorene, 10

Compound **9** (2.05 g, 6.29 mmol) and PBr_3 (10 mL, 0.11 mol) were mixed together and heated at 80 °C for 1 h. The reaction mixture was hydrolysed on ice, and then washed with diethyl ether (3 × 30 mL). The ethereal extracts were washed with water (4 × 20 mL), until the water phase reached an almost neutral pH. Hence, the ethereal solution was dried over Na_2SO_4, filtered and finally dried *in vacuo*. Compound **10** (2.06 g, 81% yield) was obtained as a microcrystalline colourless material. Anal. Calcd. for $C_{13}HBrF_8$: C, 40.13, H, 0.26. Found C, 40.22, H, 0.21%. ^{1}H NMR ($CDCl_3$): δ 6.14 (s, 1 H, CH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 3 for the fluorine atoms numbering): δ −133.8 (m, 2 F, F1 + F8); −137.2 (d, $^3J_{FF}$ = 19 Hz, 2 F, F4 + F5); −150.5 (m, 2 F, F2 + F7); −152.5 (m, 2 F, F3 + F6) ppm.

4.6. Preparation of 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,7,7′,8,8′-hexadecafluoro-9,9′-bifluorenyl, 11

A solution of **10** (1.98 g, 4.89 mmol), in diethylether (50 mL), was treated at room temperature with a 1.0 M solution of *sec*-butylmagnesium chloride in diethylether (9.80 mL, 9.80 mmol). After stirring for 2 h at room temperature, the reaction mixture was hydrolysed with ice and then treated with CH_2Cl_2 (*ca.* 500 mL). The organic phase was isolated and dried over Na_2SO_4, hence the solvent was removed *in vacuo*. The resulting residue was dissolved in toluene at *ca.* 60 °C, then the solution was filtered through Celite/activated carbon, and finally cooled to room temperature. Well-shaped crystals formed, and these were isolated by filtration and dried *in vacuo*. Yield: 1.93 g, 64%. Anal. Calcd. for $C_{26}H_2F_{16}$: C, 50.51, H, 0.33. Found C, 50.41, H, 0.37%. ^{1}H NMR ($CDCl_3$): δ 5.40 (s, 2 H, CH) ppm. ^{19}F NMR ($CDCl_3$, see Scheme 3 for the fluorine atoms numbering): δ −133.2 (m, 4 F, F1 + F8 + F1′ + F8′); −138 to −142 (d, $^3J_{FF}$ = 19 Hz, F4 + F5 + F4′ + F5′); −151.6 (m, 4 F, F2 + F7 + F2′ + F7′); −152.7 (m, 4 F, F3 + F6 + F3′ + F6′) ppm.

4.7. Crystal structure solution and refinement of compounds 1, 8, and 11

Data were collected at 293 K on a Bruker P4 diffractometer, operating with a graphite-monochromated Mo-K_α radiation. Colourless prisms of **1** or **11** or colourless platelets of **8** were glued on the tip of a glass fiber for lattice parameters and intensity data collection. The results are summarized in Table 4. The intensity data collection was carried out with the $\omega/2\theta$ scan mode; three standard reflections being measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarization effects. An absorption correction by the ψ-scan method [25] was applied only to the intensities of compound **8**. The structure solutions was obtained by direct methods [26] and refined with full-matrix least-squares on F^2 [26]. Some other utilities contained in the WINGX suite [27] were also used.

The structure solution was obtained in the centrosymmetric *C*2/*c* space group for compounds **1** and **8** and in the $P2_1/c$ space group for compound **11**. The asymmetric unit of **1** contains half molecule riding a twofold axis. Either in **1** or in **8** or in **11** the hydrogen atoms were localized in the difference Fourier map and refined without constraints. The reliability factors resulting from the final refinement cycle are listed in Table 4.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: CCDC

Table 4
Crystal data for compounds **1**, **8** and **11**.

Compound	1	8	11
Empirical formula	$C_{19}HF_{13}$	$C_{13}H_2F_8$	$C_{26}H_2F_{16}$
F W	476.20	310.15	618.28
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
a/Å	23.630(1)	16.703(3)	6.992(1)
b/Å	9.950(1)	7.650(1)	15.802(1)
c/Å	15.955(2)	8.864(1)	19.256(2)
β/°	117.86(1)	111.03(1)	98.48(1)
U/Å^3	3316.5(6)	1057.2(3)	2104.3(4)
Z	8	4	4
*D*calc/Mg m^{-3}	1.907	1.949	1.952
μ/mm^{-1}	0.214	0.213	0.214
No. collected	3549	1185	4080
No. unique [R_{int}]	2920 [0.0212]	923 [0.0373]	2930 [0.0180]
No. parameters	294	101	387
R_1, wR_2 [$I > 2\sigma(I)$]	0.0407, 0.0820	0.0346, 0.0875	0.0346, 0.0760
R_1, wR_2 [all data]	0.0777, 0.0978	0.0570, 0.0986	0.0537, 0.0843
Goodness of fit on F^2	1.012	1.048	1.015

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2, 0) + 2F_c^2]/3$; goodness-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where *N*, *P* are the numbers of observations and parameters, respectively.

No. 280475, 1,2,3,4,5,6,7,8-octafluorofluorene, 1, CCDC No. 280473, 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluorophenyl)fluorene, 8, and CCDC No. 280474, 1,1′,2,2′,3,3′,4,4′,5,5′,6,6′,7,7′,8,8′-hexadecafluoro-9,9′-bifluorenyl, 11. Copies of the crystallographic data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 123 336033 e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2008.12.011.

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