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Do fluorine atoms attached to sp^2-hybridized carbon atoms hinder electrophilic addition to the C=C bond?

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Abstract

Interaction of mercuric trifluoroacetate with 2,3-difluorobicyclo[2.2.1]hepta-2,5-diene (**I**) in a non-polar medium leads to adduct **IIa**, formed as a result of *exo–cis*-addition of the salt to the FC=CF bonds of two diene molecules. Under the action of mercuric acetate in acetic acid, diene **I** gives an *exo–cis*-adduct to the FC=CF bond (**IIb**) as well as one to the HC=CH (**IIc**) in a 3:2 ratio. Adduct **IIb** reacts with excess $Hg(OCOCH_3)_2$ and isomerizes to the tricyclic *exo,exo*-adduct **IId**.

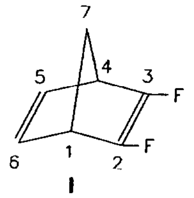
Diene **IV**, i.e. 2,3-difluoro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene, reacts with anhydrous CF_3COOH adding two molecules of the acid non-stereospecifically to both double bonds, and giving a mixture of isomeric bis-adducts **V**. A mixture of the monoadducts to the FC=CF and HC=CH bonds is formed in a 1:1.7 ratio when **IV** interacts with CF_3COOH in CH_2Cl_2. It is notable that addition to the FC=CF bond leads to the *exo*-trifluoroacetate **VIa** whereas reaction with the HC=CH bond gives a mixture of *exo-* and *endo*-trifluoroacetate, **VIb** and **VIc**.

The relative activities of the double bonds in **I** and **IV** are discussed.

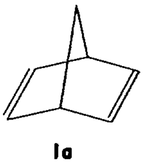
Introduction

For many years, Knunyants and his co-workers paid great attention to researches in the field of fluoro-olefin chemistry. Indeed, these compounds became one of the main subjects of their investigations. A comparison of the properties of fluoro-olefins with those of their non-fluorinated analogues has led to the formulation of the empirical rule: as the number of fluorine atoms attached to the C=C bond increases, the ability of the bond to react with nucleophilic reagents also increases, whereas its reactivity towards electrophiles decreases [1].

Recently, we have synthesized 2,3-difluorobicyclo[2,2,1]-hepta-2,5-diene (**I**), a suitable model compound for the comparison of the reactivity of a HC=CH group with that of a CF=CF group in the same molecule. Compound **I** is a simple analogue of norbornadiene (**Ia**) which has been studied in detail over many decades.

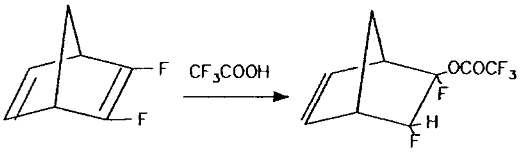


I



Ia

We have shown [2] that diene **I** is quite susceptible towards electrophilic reagents, but inert towards nucleophilic ones (it does not react with NaCN in DMF nor C_2H_5ONa in boiling C_2H_5OH). Thus, trifluoroacetic acid adds rapidly to **I** at room temperature. The stereochemistry of the reaction is the same as in the case of **Ia** [3] with the *exo-cis*-adduct **Ib** (93%) being formed. Attack is directed towards the double bond attached to the fluorine atoms:



I **Ib** (1)

This result appears to be paradoxical from the traditional points of view mentioned above. It has prompted us to investigate this reaction and the corresponding acetoxymercuration in greater detail.

Results and discussion

Diene **I** adds mercuric trifluoroacetate in chloroform readily to form the sole product **IIa**. The stereochemistry of the reaction is similar to that for the interaction of

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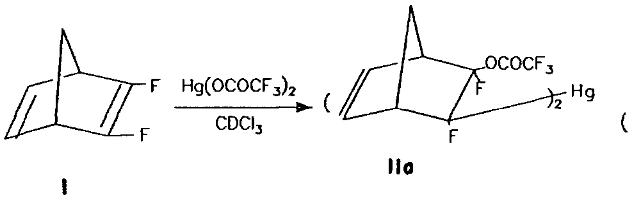
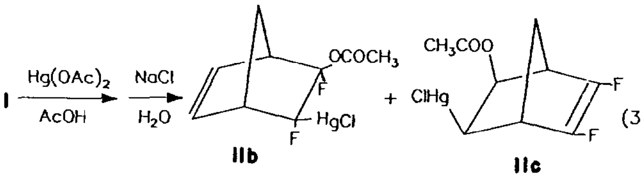
I with trifluoroacetic acid as well as for the acetoxymercuration of **Ia** [4]:



(2)

The symmetrical organomercuric compound **IIa** is not particularly stable. Its structure has been confirmed by the ^{1}H and ^{19}F NMR spectra which are quite similar to those for the non-symmetrical analogue **IIb** (see Table 1). The only essential difference noted was in the coupling constants for interaction between the F2 atom and the ^{199}Hg isotope attached to the same carbon atom. This constant is substantially smaller in the case of **IIa** (685 Hz in contrast to 1161 Hz in **IIb**).

Reaction of **I** with an equivalent amount of mercuric acetate in CH_3COOH leads to the formation of two *exo-cis*-adducts in a *c.* 3:2 ratio:

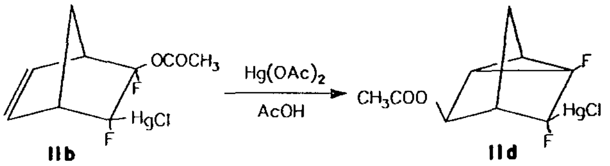


(3)

The product **IIc** also proved to be insufficiently stable to allow isolation and was characterized by physical methods. The band at 1722 cm^{-1} in the IR spectrum of **IIc** (FC=CF) as well as NMR spectral data (see Table 1) allowed consideration of the structure. Unfortunately, overlapping of the signals in the ^{1}H NMR spectrum prevented a measure of the coupling constant for interaction between the H6 proton and ^{199}Hg. However, the presence of long-range (via 4 bonds) interaction between F2 and the isotope ^{199}Hg ($J = 107$ Hz) demonstrates the position of the Hg atom indicated out. The value of the coupling constant J(H5–H6) = 6.8 Hz confirms the *cis* location of these protons: the *trans* constants J(H5–H6) in the ^{1}H NMR spectra of similar bicycles are substantially smaller as a rule [4, 5].

In discussing the NMR spectra of **IIa, b, d** (see below), it is useful to note the typical coupling constants for the long-range interaction between fluorine nuclei in *endo*-positions and protons located at C7 in an *anti*-position towards them (H7a), 'W-system' (see ref. 6), i.e. 8–10 Hz (F2) and 6–7 Hz (F3). The AB-system at *c.* 6.5 ppm in the ^{1}H NMR spectra is also quite typical. The chemical shift for this system, J(A–B), which is equal to *c.* 6 Hz, and the values of the constants J(H5–H4) and J(H6–H1) which are equal to *c.* 3 Hz, confirm the presence of the HC=CH group in norbornes no less reliably than the band at *c.* 1580 cm^{-1} in the Raman spectra.

Like its non-fluorinated analogue, compound **IIb** isomerizes to give the tricyclic adduct **IId** under the influence of excess mercuric acetate:



(4)

TABLE 1. Parameters of the NMR spectra of compounds **I** and **IIa–d**

Comp. No.	Chemical shifts δ (ppm)								
	F2	F3	H1	H4	H5	H6	H7s	H7a	CH$_3$
I	70.8		3.27		6.98		2.17	2.39	–
IIa	83.3	39.3	(3.3,	3.76)	6.33^a		1.54	1.88	–
IIb	66.4	39.2	(3.42,	3.86)	6.35^a		1.69	1.89	2.08
IIc	73.9	69.6	(2.92,	3.10)	5.3	3.1	1.7	1.96	2.11
IId^b	84.8	49.9	(3.44,	3.82)	3.24	5.38	2.06	2.21	2.14

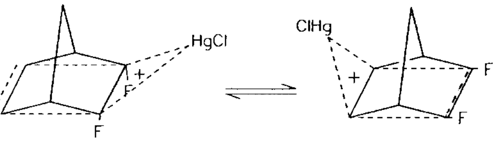
Comp. No.	Coupling constants (Hz)								
	F2F3	F2Hg	F2H1	F3H4	F2H7s	F2H7a	F3H7a	H5H6	H7sH7a
I	–	–	–	2	4	–	–	6.1	–
IIa	11.5	685	–	–	–	10.5	6.5	5.8	10.5
IIb	9.7	1161	1.5	–	2.2	9.1	6.9	5.5	10.5
IIc	–	107	2	1.4	–	5.4	4.8	6.8	11.0
IId	15.6	1075	–	2.0	–	8.5	6.8	6.8	3.1

^{a}AB-system centre.
^{b}Substance was insoluble in $CDCl_3$. Its spectra were recorded in $(CD_3)_2CO$.

The direct formation of **IId** also takes place when **I** interacts with excess mercuric acetate; **IId** was isolated as a product of this reaction.

Arguments for the formula given for **IId** are the absence of the band characteristic for the C=C bond in its Raman spectrum and the loss of the peak corresponding to the ion with $m/z = 66$ (molecular ion of cyclopentadiene, CP). Such a peak appears in the mass spectra of norbornenes containing a non-substituted CP fragment as a result of retrodiene reaction [7]. The chemical shift of the H6 proton (5.98 ppm, [4]) confirms the *exo*-position of the acetate group at the same carbon atom in the molecule of **IId**.

Evidently the tricyclic adduct **IId** is the final thermodynamic product of acetoxymercuration of **I** to the FC=CF bond, while **IIb** and **IIc** are kinetic products. They are probably formed a s a result of the recombination of an acetate ion with the intermediate mercurinium ion $\mathbf{II}^+$, the latter being capable of existing in two equilibrium forms:

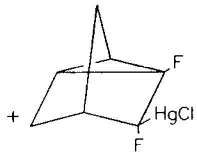


(5)

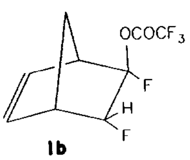
$\mathbf{IIa}^+$ $\mathbf{IIc}^+$

A similar ion was registered in the NMR spectra during the action of the CH_3Hg^+ cation on **Ia** in an SO_2 medium [8].

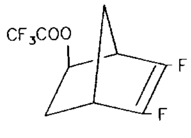
Both acetic acid and sodium acetate are incapable of catalyzing the isomerization of **IIb** to **IId**. The action of mercuric acetate probably increases the reversibility of recombination between $\mathbf{II}^+$ and AcO^-. As a result, the opportunity for a slow but irreversible isomerization of cation $\mathbf{IIa}^+$ to the tricyclic form $\mathbf{IId}^+$ arises:



Thus acetoxymercuration of **I** proved to be less selective than the addition of CF_3COOH. To explain the specific features of the chemical behaviour of **I** we have carried out quantum-mechanical computations for the **I** and **Ia** molecules and for the isomeric adducts of **I** with CF_3COOH (**Ib**, **Ic**):



Ib



Ic

Cations $\mathbf{IIa}^+$ and $\mathbf{IIc}^+$ have also been computed via the MNDO method [9] on the basis of the MOPAC program [10] with optimization of geometry (IBM PC AT 386/387). The results of these computations lead to the following conclusions:

1. In unsubstituted norbornadiene (**Ia**), two upper occupied MOs with energies of −9.81 and −9.48 eV, respectively, in the main include π-AOs of carbon atoms (at C=C bonds) (cf. ref. 11). In the molecule of **I**, the MO localized at atoms of the FC=CF fragment, with $E = -6.63$ eV, becomes the highest occupied MO. The other boundary orbital of π-type, which lies 0.54 eV below, is localized at the carbon atoms of the HC=CH fragment. Such structures for the two upper occupied MOs favour electrophilic addition to the FC=CF bond. However, soft electrophilic agents which are sufficiently active, for example $Hg(OAc)_2$ in an ionizing medium, are capable of forming adducts with both the double bonds.

The calculated heat of formation of **I** (ΔH_f) is equal to -138.1 kJ mol^{-1} and the dipole moment has a value of 3.2 D. The magnitude of the later value is sufficiently large to make it the cause of the higher boiling point of **I** (112–113 °C) relative to that of **Ia** (90.3 °C) [12].

Computations of the bond lengths of the **I** molecule (see Table 2) show that they differ slightly from those in the unsubstituted analogue **Ia** (see ref. 13). The introduction of fluorine atoms into a position α to the C=C bond affects the charge distribution. However, according to our experiments, this distribution does not play a determining role in the interaction of **I** with electrophilic reagents which is subjected to the orbital control: the C5 and C6 atoms bearing a noticeable negative charge (−0.1) are not the sites which are first attacked.

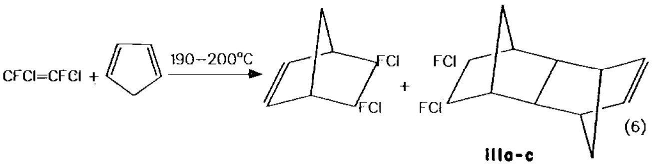
2. It is shown that the *cis*-adduct **Ib** is more stable than its isomer **Ic** by *c.* 30 kJ mol^{-1} (for both the *endo* and *exo* forms).

3. The cation $\mathbf{IIa}^+$ is also more stable (by 22.6 kJ mol^{-1}) than its isomer $\mathbf{IIc}^+$. Calculations demonstrate for the former the unusual opportunity of coordination of the Hg^{2+} cation with the unshared electron pairs of the fluorine atoms. We intend to investigate this in more detail later.

TABLE 2. Bond lengths (Å) and atomic charges (a.u.) calculated for molecule **I**

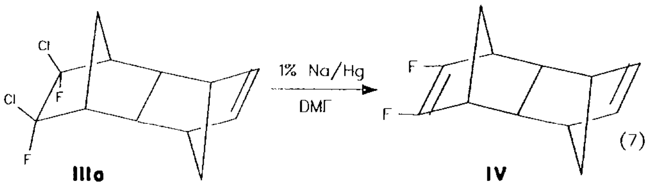
C1−C2	1.551	C5−C6	1.357	C1	0.01
C2−C3	1.383	C1−H	1.101	C2	+0.06
C1−C7	1.579	C2−F	1.310	C5	−0.10
C1−C6	1.539	C5−H	1.096	C7	−0.01
		C7−H	1.115	F	−0.15

The orientation of electrophilic addition to **I** can hardly be considered to be a measure of the comparative activity for HC=CH and FC=CF bonds, because the π-orbitals in the molecule are obviously not independent of each other. To achieve a more unambiguous comparison, we have studied a similar diene with the double bonds isolated. Such a diene was obtained by dechlorination of the by-products of the Diels–Alder reaction of CP with 1,2-dichlorodifluoroethylene. The latter reaction has been reported as giving only a mixture of isomeric 1:1 adducts [14], but we have found that these adducts are capable of adding a second CP molecule under the same conditions:



IIIa-c (6)

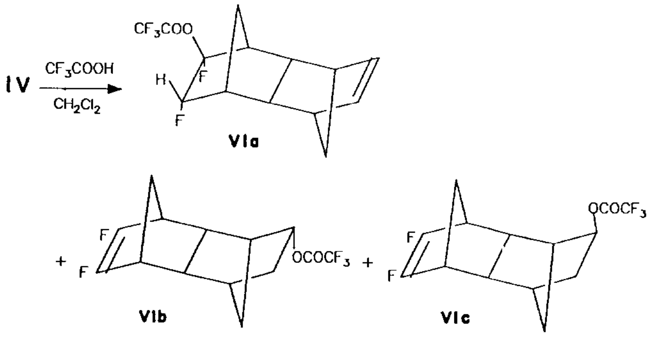
The pure *exo,cis*-isomer **IIIa** was isolated from the mixture of dichlorides **III** by crystallization. The structure of **IIIa** has been confirmed by X-ray investigation (see below). Under the action of sodium amalgam, **IIIa** gives the required diene **IV** [eqn. (7)].



IIIa **IV** (7)

Diene **IV** reacts readily with anhydrous CF_3COOH in a similar fashion to diene **I**, but forms the product arising from acid addition to both double bonds (**V**). Such addition is not stereospecific. ^{19}F and ^1H NMR spectroscopy has shown that four isomers exist in the mixture as a result of both *cis*- and *trans*-addition to the HC=CH and FC=CF bonds.

Under mild conditions, CF_3COOH diluted with CH_2Cl_2 reacts with **IV** at a slower rate. Only signals corresponding to the three isomeric monoadducts were found for such a solution 2h after mixing the reagents. We have managed to isolate this mixture (which is sensitive to both O_2 and atmospheric moisture) in 36% total yield.



VIa

VIb **VIc**

It is remarkable that, in this case, addition to the FC=CF bond is stereospecific; like diene **I**, diene **IV** forms the *exo,cis*-adduct **VIa** whereas the HC=CH bond reacts less selectively. Addition to the latter bond results in the formation of *exo*- (**VIb**) and *endo*-trifluoroacetate **VIc** in a 1.4:1 ratio. The absence of selectivity appears to be explained by the higher activity of the HC=CH bond (in comparison with the activity of FC=CF) in the molecule **IV**: the total amount of **VIb**+**VIc** is 1.7-times that of **VIa** in the mixture. This value may be considered a measure of the stability of the double bond towards hard electrophilic reagent as a result of the introduction of two fluorine atoms.

However, this value can hardly be regarded as a general characteristic. It is most likely to change depending on the structure of a molecule and the nature of the reagents acting on it. Nevertheless, the basic tendency formulated in the above empirical rule has been confirmed. Fluorine atoms attached to sp^2 carbon atoms substantially decrease the activity of the double bond towards electrophilic reagents. However, in some cases, such a decrease may only be marginal. The negative inductive effect of fluorine atoms is compensated to a significant extent by the influence of their occupied p-orbitals.

Experimental

^1H and ^{19}F NMR spectra were recorded with a Bruker AC-200 X instrument (200 MHz for ^1H and 188.3 MHz for ^{19}F), chemical shifts are given in ppm relative to TMS and CF_3COOH respectively, coupling constants are given in Hz. NMR data for most of the new compounds are listed in Tables 1 and 3. IR spectra were recorded on a UR-20 spectrometer and Raman spectra on a Ramanor HG-2S spectrometer employing a 100 mW power Ar^+ laser ($\lambda = 5145$ A, $P \sim 100$ mW), using $CDCl_3$ as the solvent except in the special case pointed out. Mass spectra were obtained on a YGMS 7070E spectrometer (ionizing electron energy, 70 eV; m/z listed).

Acetoxymercuration of I

$Hg(OAc)_2$ (1.58 g, 5 mmol) was added to a solution consisting of 0.58 g (4.5 mmol) diene **I** in 10 ml glacial AcOH. After 24 h, the solution was poured into 10 ml of 8% aqueous NaCl solution and extracted twice with CH_2Cl_2. The extracts were washed with water, dilute $NaHCO_3$ solution, water again and dried with $MgSO_4$. After evaporation *in vacuo*, 1.8 g (94%) of a white material was obtained, which gave **IIb** (m.p. 114–116 °C) and **IId** (m.p. 144–145 °C, decomp.) either by crystallization from benzene (**IId**) or from a benzene/hexane mixture (**IIb**).

TABLE 3. Parameters of NMR spectra for compounds **IIIa** and **IV**

Comp. No.	Chemical shifts δ (ppm)							
	F	H1, H4	H4a, H8a	H5, H8	H6, H7	H9	H10s	H10a
IIIa	40.8	2.70	2.81	2.98	6.03	1.54	1.24	2.60
IV	74.9	2.76	2.80	2.88	6.04	1.69	2.25	2.59

Comp. No.	Coupling constants (Hz)						
	FH10s	FH10a	H1(H4)H10	H1H8a(H4H4a)	H9sH9a	H9H5	H10sH10a
IIIa	2.6	7.2	2.3	2.2	8.6	1.6	12.5
IV	3.0	6.1	–	–	7.8	1.2	9.4

[a] AB-system centre.
[b] For parameters for non-substituted hydrocarbon, see ref. 15.

Compound **IIb**: Raman (ν, cm^{-1}): 1582. MS (measured on the ^{202}Hg, ^{35}Cl isotopes): 364 $(M-CH_3COOH)^+$; 187 $(M-HgCl)^+$; 128 $C_7H_6F_2^+$; 66 $C_5H_6^+$. Analysis: Found: Hg, 47.1%. $C_9H_9ClF_2HgO_2$ requires: Hg, 47.3%.

The mass spectrum of **IId** was similar to that given above, but contained no ion peak corresponding to $m/z = 66$. Analysis: Found: Hg, 48.5%.

2,3-Dichloro-2,3-difluoro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalenes IIIa–c

A mixture consisting of 37 g (0.57 mol) dicyclopentadiene, 143 g (1.07 mol) 1,2-dichlorodifluoroethylene (as a mixture of *cis*- and *trans*-isomers) and 0.5 g hydroquinone was heated in a steel autoclave (200 ml capacity) for 15 h at 190–200 °C. Excess volatile substances were distilled off into a trap cooled to −78 °C. Distillation of the residue gave 46 g (41% per amount of CP taken) of a mixture of isomeric 2,3-dichloro-2,3-difluorobicyclo-[2.2.1]hept-5-enes (b.p. 78–80 °C/10 mmHg) and 21 g (14%) of mixture **IIIa–c** (b.p. 125–126 °C/1 mmHg). ^{19}F NMR δ: for the mixture: 13.4 and 30.3 (1:1, *trans*-isomer); 31.6 (*endo,cis*-dichloride); and 40.8 (*exo,cis*-dichloride) ppm. Relative content, 54:14:32.

Pure **IIIa** (m.p. 79–80 °C) was isolated by crystallization from hexane at −78 °C, then from alcohol/water. Raman (ν, cm^{-1}): 1571 (C=C). Analysis: Found: C, 54.24; H, 4.48; F, 14.41%. $C_{12}H_{12}F_2Cl_2$ requires: C, 54.36; H, 4.56; F, 14.33%.

2,3-Difluoro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (IV)

Dichloride **IIIa** (2.2 g, 8.4 mmol) in 12 ml dry DMF was stirred for 7 h with 97 g 1% Na/Hg. The amalgam was separated, the solution poured into water and extracted with CH_2Cl_2. After drying and evaporation of the solvent, distillation gave 1.15 g (70%) **IV** (b.p. 66–67 °C/1 mmHg). IR (cm^{-1}): 1722 (FC=CF). Raman (ν, cm^{-1}): 1575 (HC=CH). Analysis: Found: C, 74.01; H, 6.19; F, 19.58%. $C_{12}H_{12}F_2$ requires: C, 74.20; H, 6.23; F, 19.57%.

Addition of trifluoroacetic acid to diene IV

Method A

Diene **IV** (0.6 g, 3 mmol) was dissolved in 5.3 g anhydrous CF_3COOH. After 24 h, the solution was poured into water and treated as described for the products of **I** acetoxymercuration. A viscous liquid **V** (0.65 g, 51%) was obtained (b.p. 145–146 °C/2 mmHg). ^{19}F NMR spectroscopy indicated four singlets with δ of *c.* −2 ppm (6F), four d d (br) with d *c.* 54 ppm ($^1J = 8$–9 Hz, $^2J = 6$–7 Hz in every d d, 1F), 2 d with δ 121.6 and 122.1 ppm (intensity ratio, 1.8:1) ($J_{F-H} = 51.5$ Hz, 1F). There were signals 4.83 and 4.97 ppm (*exo*-H–C–OAc, two isomers) as well as 4.56 and 4.59 ppm (*endo*-H–C–OAc) in the ^{1}H NMR spectra. Analysis: Found: C, 45.76; H, 3.46; F, 35.55%. $C_{16}H_{14}F_8O_4$ requires: C, 45.51; H, 3.34; F, 36.00%.

Method B

A solution consisting of 1 g (5 mmol) **IV** in 1 ml of dry CH_2Cl_2 was added to a solution of dry CF_3COOH (2.9 g, 25 mmol) in 3 ml CH_2Cl_2. After 2 h, the mixture was treated in the same manner as above and 0.55 g (36%) of a viscous oil **VI** was isolated (b.p. 98–100 °C/1 mmHg). IR (cm^{-1}): 1578 (vw) (HC=CH); 1722 (m) (FC=CF); 1780 (s) (CF_3COO at CH); 1802 (s) (CF_3COO at CF). ^{19}F NMR spectroscopy indicated δ of −2 (s 3F); 73.3 (br s) and 75.3 (br s) (1:1); 73.8 (br s) and 74.4 (br s) (1:1) (intensity ratio of pairs, 1.4:1); 124.4 (d) ($J_{F-H} = 51.5$ Hz) ppm, which corresponds in intensity to the δ 55.5 (br m) ppm sum of the six 2F signals. The intensity of the sum of the first four signals (corresponding to the vinyl fluorine atoms) exceeded the intensities of the last two signals by 1.7-

TABLE 4. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for compound **IIIa**

Atom	*x*	*y*	*z*	*U*
Cl(C2)	9869(1)	3908(1)	1590(1)	37(1)[a]
F(C2)	10833(1)	3641(1)	4136(1)	33(1)[a]
C(1)	8733(2)	3541(2)	4280(2)	25(1)[a]
C(2)	9850(1)	3229(1)	3433(2)	24(1)[a]
C(7)	6848(2)	3108(2)	6740(2)	34(1)[a]
C(8)	8028(2)	3530(2)	7223(2)	33(1)[a]
C(8a)	8937(2)	3216(2)	5964(2)	25(1)[a]
C(9)	8321(3)	2500	8351(3)	40(1)[a]
C(10)	7974(2)	2500	3660(3)	27(1)[a]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*(*i*, *j*) tensor.

TABLE 5. Bond angles (°) for compound **IIIa**

Cl(2)−C(2)−F(2)	105.2(1)	C(1)−C(8a)−C(8)	121.6(1)
Cl(C2)−C(2)−C(1)	111.0(1)	C(1)−C(8a)−C(4a)	103.3(1)
F(C2)−C(2)−C(1)	114.5(1)	C(8)−C(8a)−C(4a)	102.6(1)
Cl(C2)−C(2)−C(3)	114.6(1)	C(8a)−C(8)−C(7)	110.4(2)
F(C2)−C(2)−C(3)	109.1(1)	C(8a)−C(8)−C(9)	98.4(2)
C(1)−C(2)−C(3)	102.8(1)	C(7)−C(8)−C(9)	99.2(2)
C(2)−C(1)−C(8a)	106.5(1)	C(6)−C(7)−C(8)	107.8(1)
C(2)−C(1)−C(10)	98.7(1)	C(1)−C(10)−C(4)	95.2(2)
C(8a)−C(1)−C(10)	105.0(1)	C(8)−C(9)−C(5)	94.0(2)

TABLE 6. Hydrogen coordinates ($\times 10^3$) and temperature factors ($Å^2 \times 10^2$) for compound **IIIa**

Atom	*x*	*y*	*z*	*U*
H(1)	848(2)	436(2)	412(2)	3(1)
H(7)	628(2)	359(2)	639(2)	4(1)
H(8)	809(2)	435(2)	755(2)	3(1)
H(8a)	966(2)	350(2)	630(2)	3(1)
H(91)	912(3)	250	872(4)	4(1)
H(92)	783(3)	250	922(4)	4(1)
H(101)	714(3)	250	403(3)	3(1)
H(102)	794(3)	250	256(4)	4(1)

times. The existence of an AB-system (centre 6.04, $J_{AB} = 6$ Hz); 4.54 (d) (HCF); and 4.79 (br d) and 5.03 (br d) (1:1.4) ($J = 6$ Hz) ppm was demonstrated in the ^{1}H NMR spectrum. Analysis: Found: C, 54.51; H, 4.30%. $C_{14}H_{13}F_8O_2$ requires: C, 54.55; H, 4.25%.

X-Ray investigation data for compound IIIa

Crystals of **IIIa** are orthorhombic, at −120 °C: $a = 11.647(5)$, $b = 10.917(5)$, $c = 8.792(3)$ Å, $V = 1118(2)$ Å^3. Space group Pnma, $Z = 4$ (molecule in the mirror symmetry plane), $d_c = 1.58$ g cm^{-3}.

Unit cell parameters and intensities for 1315 reflections with $I > 3\sigma$ were measured with an automated Siemens P3/PC diffractometer (MoKα, $2\Theta/\Theta$ scan, $\Theta < 28°$). The structure was solved by direct methods. Hydrogen atoms were located via a difference synthesis of the electron density. Refinement of the structure in the anisotropic (isotropic for hydrogen atoms) approximation converged to $R = 0.034$, $Rw = 0.033$. The coordinates of the non-hydrogen atoms and their equivalent isotropic temperature factors are listed in Table 4, the bond angles in Table 5 and the coordinates of the hydrogen atoms in Table 6.

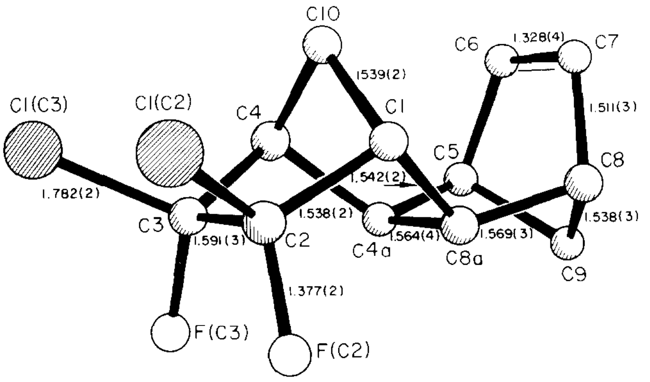


Fig. 1. Molecular structure of compound **IIIa**.

Figure 1 shows a perspective view of molecule **IIIa** including atom numbering and bond lengths. The molecule is located on the symmetry plane passing through the C9 and C10 atoms and the mid-points of the C2−C3, C4a−C8a and C6−C7 bonds.

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