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Skeletal transformations of perfluoro-1-ethyl-1-phenylbenzocyclobutene in the reaction with antimony pentafluoride

Tatyana V. Mezhenkova, Victor M. Karpov *, Vyacheslav E. Platonov, Yuri V. Gatilov

N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia

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Dedicated to the memory of Professor G.G. Yakobson on the occasion of his 80th birthday (1928–1984).

ABSTRACT

Interaction of perfluoro-1-ethyl-1-phenylbenzocyclobutene with SbF_5 at room temperature gives, after treatment of the reaction mixture with H_2O, perfluoro-4-[1-(2-methylphenyl)propylidene]cyclohexa-2,5-dienone as a main product. The reaction at 90–95 °C leads, after treatment with H_2O, to a mixture of perfluorinated 9-ethyl-9-methyl-1,2,3,4-tetrahydro-9*H*-fluorene, 9-ethyl-4a-methyl-4,4a-dihydrofluoren-1-one, 3-ethyl-3-phenylphthalide, 1-hydroxy-2-methyl-1-phenylindan, 3-methyl-2-phenylindenone and small amounts of other products.

1. Introduction

In the hydrocarbon series cationoid rearrangements are widespread, whereas in the series of perfluorinated compounds they occur very rarely [1,2]. There was reported in the literature the alicyclic ring contraction of 2-halopolyfluorotetralins in the reaction with SbF_5 [3] and the ring opening of perfluorocyclopropane derivatives under the action of antimony pentafluoride [4] or aluminium chlorofluoride [5]. Skeletal transformations of perfluorobenzocycloalkenes (benzocyclobutene, indan and tetralin) and their perfluoroalkyl and perfluoroaryl derivatives in the reactions with antimony pentafluoride have been investigated by us [6–15]. Thus, perfluoro-1-methyl- and 1-ethylbenzocyclobutenes undergo expansion of the four-membered ring to form polyfluoroindans [6]. The mechanism of the process differs from that for the non-fluorinated analogues [16]. The alicyclic ring cleavage of perfluorodialkylbenzocyclobutenes leads to polyfluorostyrenes, which subsequently undergo cyclization into polyfluoroindans or fluorination to perfluoro-*ortho*-dialkylbenzenes [9,10]. Perfluoro-1-(2- or 4-ethylphenyl)benzocyclobutenes when heated with SbF_5 give the products of alicyclic ring opening, which then convert to polyfluorinated fluorene or anthracene derivatives. In contrast to this, perfluoro-1-phenylbenzocyclobutene does not undergo skeletal transformations under the same conditions [13]. Perfluoro-1,2-diethyl-1-phenylbenzocyclobutene in mild conditions undergoes four-membered ring opening along with alicyclic and pentafluorobenzene rings expansion leading to polyfluorobenzoazulene derivatives [15].

In order to establish the common regularities of cationoid skeletal transformations of polyfluorobenzocyclobutenes, containing perfluoalkyl group together with perfluoroaryl group in the alicyclic fragment of the molecule, we have studied the reaction of perfluoro-1-ethyl-1-phenylbenzocyclobutene (**1**) with SbF_5.

2. Results and discussion

It has been shown that long standing (4 months) of benzocyclobutene **1** in an excess of SbF_5 at 20–25 °C leads, after treatment of the reaction mixture with H_2O, to perfluoro-4-[1-(6-methylphenyl)propylidene]cyclohexa-2,5-dienone (**2**) as a main product. Reaction mixture also contains perfluorinated 3-ethyl-3-phenylphthalide (**3**), 9-ethyl-4a-methyl-4,4a-dihydrofluoren-1-one (**4**) and a small amount of 9-ethyl-4a-methyl-4,4a-dihydrofluoren-3-one (**5**) (Scheme 1).

* Corresponding author. Fax: +7 3833 30 9752.
E-mail address: karpov@nioch.nsc.ru (V.M. Karpov).

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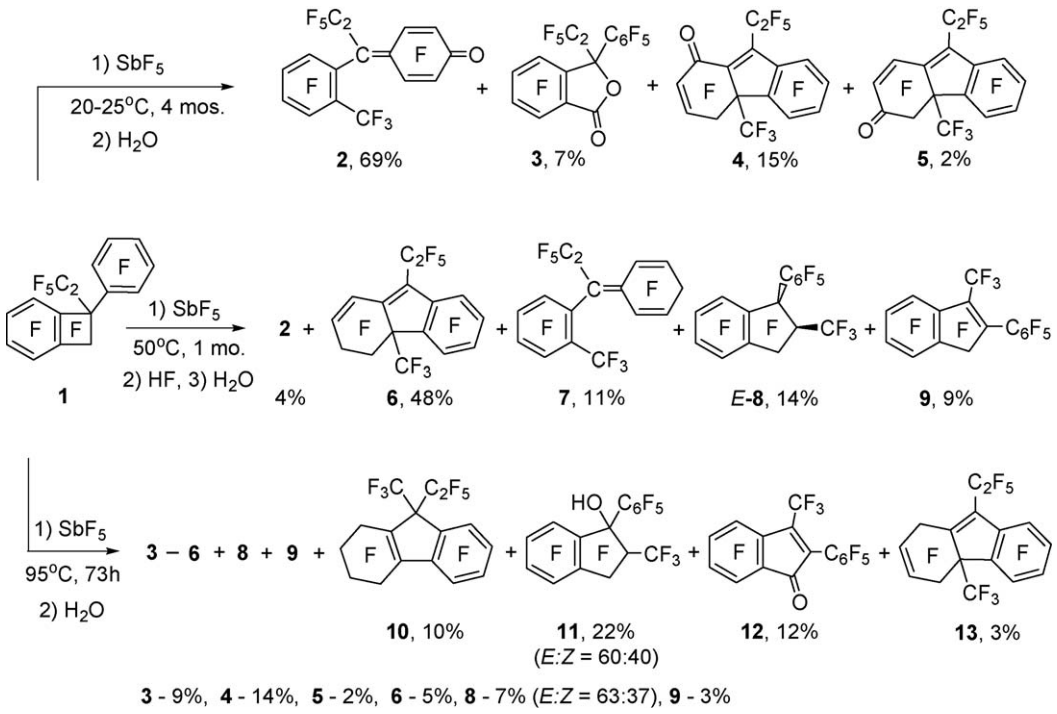
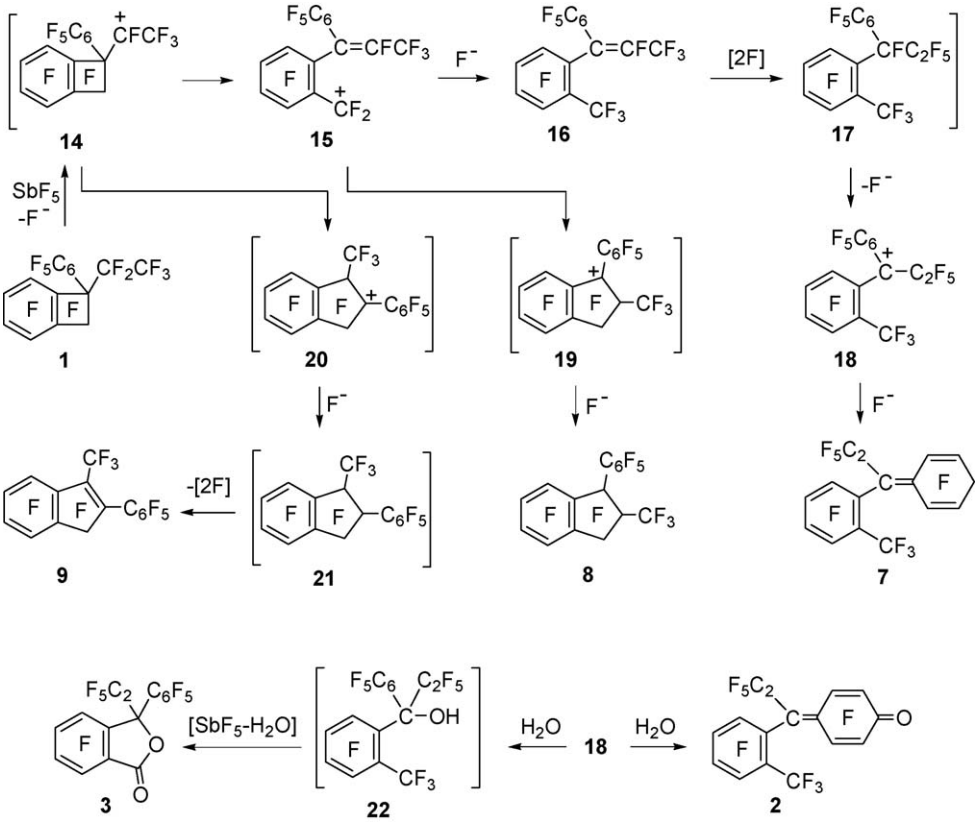
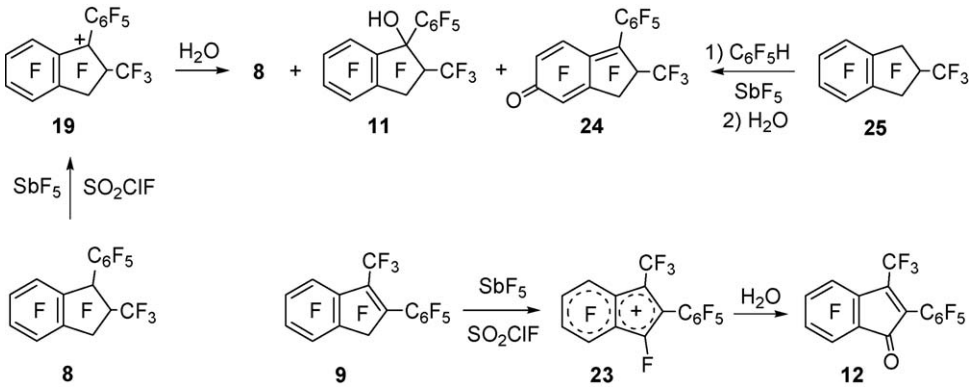


Scheme 1.

Prolonged heating of benzocyclobutene **1** with SbF_5 at 50 °C (1 month) and further treatment of the reaction mixture with anhydrous HF and then with water gives predominantly perfluoro-9-ethyl-4a-methyl-4,4a-dihydro-3*H*-fluorene (**6**) along with perfluorinated 1-[1-(cyclohexa-2,5-dienylidene)propyl]-2-methylbenzene (**7**), 2-methyl-1-phenylindan (**8**), 3-methyl-2-phenylindene (**9**) and compound **2**. The reaction at 95 °C (73 h) leads, after treatment of the reaction mixture with H_2O, to perfluoro-9-ethyl-9-methyl-1,2,3,4-tetrahydro-9*H*-fluorene (**10**), 1-hydroxyperfluoro-2-methyl-1-phenylindan (**11**), perfluoro-3-



Scheme 2.



Scheme 3.

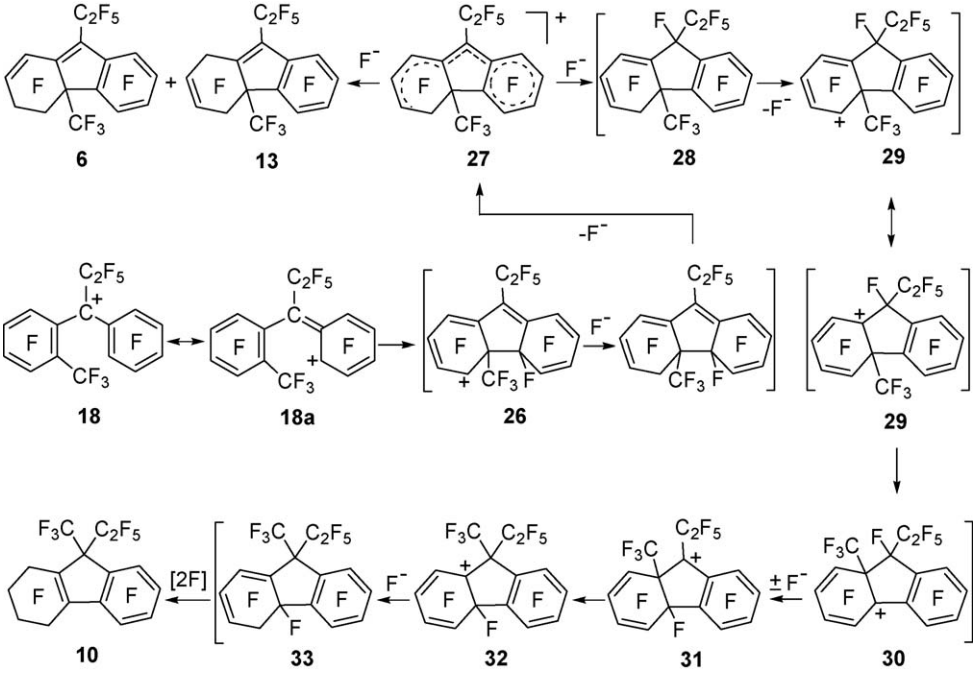
methyl-2-phenylindenone (**12**), phthalide **3**, fluorenone **4** and small amounts of compounds **5**, **6**, **8**, **9** and perfluoro-9-ethyl-4a-methyl-4,4a-dihydro-1*H*-fluorene (**13**) (Scheme 1).

Transformation of benzocyclobutene **1** to products **2**, **3**, **7**-**9** may be represented by Scheme 2. Thus, reversible elimination of the fluoride ion from compound **1** under the action of SbF_5 possibly leads to cation **14**, which undergoes alicyclic ring opening to give cation **15** and then compound **16** after the fluoride ion addition. Subsequent fluorination leads to product **17**, which under the action of SbF_5 gives perfluoro-1-(2-methylphenyl)-1-phenylprop-1-yl cation (**18**). Addition of the fluoride ion to cation **18** leads to compound **7**. On the other hand cation **15** may undergo intramolecular cyclization to form perfluoro-2-methyl-1-phenylindan-1-yl cation (**19**), which adds the fluoride ion to give indan **8**. Opening of the four-membered ring and its expansion to the five-membered one in compound **1** under the action of SbF_5 are similar to those in perfluoroalkylbenzocyclobutenes [9,10], whereas formation of indene **9** in this reaction seems to proceed another way. It may be suggested that intramolecular attack of tetrafluorobenzene ring by cationic center in cation **14** leads to indanyl cation **20**, which adds the fluoride ion to form indan **21**. The latter undergoes defluorination to give indene **9** (Scheme 2). Relative stabilities of cations **14**, **15**, **19** and **20** will be discussed below.

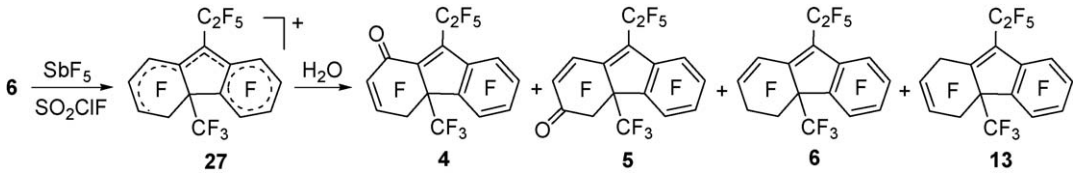
It has been shown earlier that perfluoro-1,2-dimethylindan may transform to perfluoro-2,3-dimethylindene as a result of defluorination, proceeding with participation of intermediate double bond containing particles as acceptors of fluorine atoms [10]. It is believed that in the process of defluorination of indan **21** styrene **16** may act as an acceptor of fluorine atoms (Scheme 2). Transformation of styrene **16** to compound **17** may also proceed under the action of SbF_5 as fluorination agent (cf. fluorination of fluoroolefins [17]).

Formation of cation **18** was observed in the reaction of benzocyclobutene **1** with SbF_5 at 20–25 °C. After the treatment of the solution of a salt of cation **18** with water along with ketone **2** there was obtained phthalide **3** (Scheme 2). It may be supposed that hydrolysis of cation **18** leads not only to ketone **2** but also to hydroxyderivative **22**, which transforms to phthalide **3** under the action of antimony pentafluoride and water during the aqueous treatment of the reaction mixture (cf. the formation of 3-dichloromethyleneperfluoroindan-1,2-dione together with 3-dichloromethyleneperfluoroindan-1-one (ratio, 1:1) during the aqueous treatment of a solution of a salt of 3-dichloromethyleneperfluoroindan-1-yl cation in SbF_5 [18]).

Cation **19** and perfluoro-1-methyl-2-phenylindenyl cation (**23**) have been generated from compounds **8** and **9** in the system SbF_5–



Scheme 4.



Scheme 5.

SO_2ClF. The treatment of the solutions of the salts of cations **19** and **23** with water leads to products **11** and **12**, respectively. In the case of cation **19** reaction mixture also contained precursor **8** and perfluoro-8-methyl-7-phenylbicyclo[4.3.0]nona-1,4,6-trien-3-one (**24**) (Scheme 3).

Compounds **8**, **11** and **24** have been also synthesized in a separate experiment from perfluoro-2-methylindan (**25**) and C_6F_5H in an SbF_5 medium with subsequent hydrolysis of the reaction mixture (Scheme 3).

Formation of fluorene derivatives **6**, **10** and **13** may be represented as a result of transformation of cation **18** in an SbF_5 medium (Scheme 4). At first in cation **18** there occurs aromatic ring attack by a positively charged *ortho*-carbon of the pentafluorophenyl group (resonance structure **18a**) leading to ion **26**, which then transforms into perfluoro-9-ethyl-4a-methyl-4,4a-dihydro-3*H*-fluoren-3-yl cation (**27**) by the fluoride ion addition–elimination. Cation **27** adds the fluoride ion to form compounds **6**, **13** and possibly compound **28**. Elimination of the fluoride ion from the latter gives cation **29**. Isomerization of cation **29** to **30** by CF_3 group migration and subsequent addition–elimination of the fluoride ion leads to cation **31**. The latter transforms into cation **32** by 1,2-shift of CF_3 group. The possibility of CF_3 group migration to cationic centre was discussed in relation to the route of isomerization of perfluoro-1-ethylindan to perfluoro-1,1-dimethylindan under the action of SbF_5 [8]. Addition of the fluoride ion to cation **32** leads to compound **33**, which then undergoes fluorination and isomerization with removal of the double bond to give product **10** (Scheme 4). It should be noted that compound **33** may be also regarded as an acceptor of fluorine atoms in the process of defluorination of indan **21** to indene **9**.

Cation **27** has been generated from compound **6** in the system SbF_5–SO_2ClF. The treatment of the solution of the salt of cation **27** with water leads to ketones **4** and **5** (85:15) together with small amounts of precursor **6** and its isomer **13** (60:40) (Scheme 5).

When the reaction mixture prepared by heating of benzocyclobutene **1** with SbF_5 is treated with water, compounds **4**–**6**, **13** are obtained with about the same ratio of isomers. At the same time, after treatment with anhydrous HF and then with water, the reaction mixture contains product **6** in the absence of isomer **13**. In addition, after treatment with anhydrous HF or water, the reaction mixtures contain *E*-isomer or a mixture of *E*,*Z*-isomers of compound **8**, respectively (Scheme 1).

The formation of product **6** in the absence of isomer **13** and compound *E*-**8** in the absence of isomer *Z*-**8** after quenching reaction mixture with HF is apparently a result of a thermodynamic control of the reaction. When the reaction mixture is treated with water, compounds **6** and **13**, *E*-**8** and *Z*-**8** are obtained because the equilibrium between isomers has no time to attain.

Predominance of ketone **4** as compared with isomer **5** after hydrolysis of cation **27** is apparently a result of a kinetic control of the reaction and it is in agreement with MNDO calculated distribution of positive charge on the carbon atoms (+0.505 and +0.258, respectively) in this cation.

It should be noted that gas-phase DFT (PBE/TZ2P, PRIRODA program [19]) calculations show that compound **6** is more stable by 5.1 kcal mol^{-1} than its isomer **13**, ketone **4** is less stable by 3.2 kcal mol^{-1} than its isomer **5**, and *E*-isomer of compound **8** is more stable by 2.3 kcal mol^{-1} than its *Z*-isomer.

DFT calculations of cations **14**, **15**, **19** and **20** show that cation **19** is more stable by 19.0 and 16.0 kcal mol^{-1} than cations **15** and **20**, respectively. Cation **14** has not local minimum on a potential energy surface. Therefore we have calculated perfluoro-1-acetyl-1-phenylbenzocyclobutene. The calculation has showed that this ketone has two stable conformers. Then C=O groups of both conformers of the ketone were replaced with C(+)–F and resulted structures of **14** were optimized. During optimization one conformer was transformed into cation **15** and the other was transformed into cation **20**.

The structures of compounds **2**, **4**–**8**, **10**, **11**, **13** and **24** were established by HRMS and ^{19}F NMR spectroscopy. Assignment of signals in the ^{19}F NMR spectra was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. The fine structure of signals was interpreted in approximation to the first order structure. Compounds **8** and **11** are formed as mixtures of *E*- and *Z*-isomers. The configurations of *E*- and *Z*-isomers of compound **8** were defined on the base of $J_{F(1)-CF_3(2)}$ value, which is equal to 19 Hz for *E*-isomer. For *Z*-isomer exact value of $J_{F(1)-CF_3(2)}$ cannot be measured but it does not exceed 10 Hz (cf. $J_{F(1)-CF_3(2)}$ and $J_{F(2)-CF_3(1)}$ values in polyfluoromethylindans [8,20]). The larger value of $^4J_{F(1)-CF_3(2)}$ for *E*-isomer compared with *Z*-isomer of compound **8** indicates that the interacting nuclei in *E*-isomer are closely spaced, or, in other words, that F(1) and $CF_3(2)$ are located on one side of the ring plane (see fluorine through-space coupling constants [21–23]).

The configurations of **E-11** and **Z-11** were supposed on the base of *tert*-F(2) signal chemical shift value by analogy to **8**. So, in spectrum of isomer *E*-**8** the signal of *tert*-F(2) atom, situated in *cis*-position to C_6F_5-group, is shifed downfield (−174.1 ppm) as compared with isomer *Z*-**8** (−177.5 ppm). In view of this fact *E*-configuration was attributed to that isomer of compound **11**, for which the signal of *tert*-F(2) atom is located at −171.4 ppm, and *Z*-configuration, for which *tert*-F(2) signal has chemical shift −175.8 ppm. Similar regularities were observed for *E*,*Z*-2-hydroxyperfluoro-1-methyl-2-phenylbenzocyclobutenes with configuration of *E*-isomer defined by X-ray diffraction [24].

Compounds **3**, **9** and **12** were identified by comparison of the ^{19}F NMR data with data for authentic samples [14,25]. The structures of cations **18**, **19**, **23** and **27** were identified by ^{19}F NMR spectra. The regularities in the spectra of cations **18**, **19** and **23** agree with those for polyfluorodiarylmethyl [13,26], perfluoro-1-phenylindan-1-yl [12] and polyfluoroindenyl cations [27], respectively.

The structures of compounds **2** and **4** were confirmed by X-ray crystallography (Figs. 1 and 2).

According to a single crystal X-ray structure determination the bond lengths in 4-methylenecyclohexa-2,5-dienone fragment of compound **2** are close to those in perfluoro-8-ethyl-5-phenyl-7,8-dihydronaphthalen-2(6*H*)-one [28]. The carbon atoms C3, C5, C7, C14, attached to the atoms C4 and C13, linked by a double bond, are located in two planes so that dihedral angle between the C3C4C5C13 and C4C7C13C14 planes is equal to 11.1°. Molecules of compound **2** form centrosymmetric pairs with C1···O1 distances 3.043(4) Å (the sum of the van der Waals radii is 3.35 Å [29]). It should be also noted reduced intermolecular contacts F1···F16 2.775(4) and O1···F17 2.885(4) Å (the sums of the van der Waals radii are 2.92 and 3.04 Å, respectively [29]) between pairs.

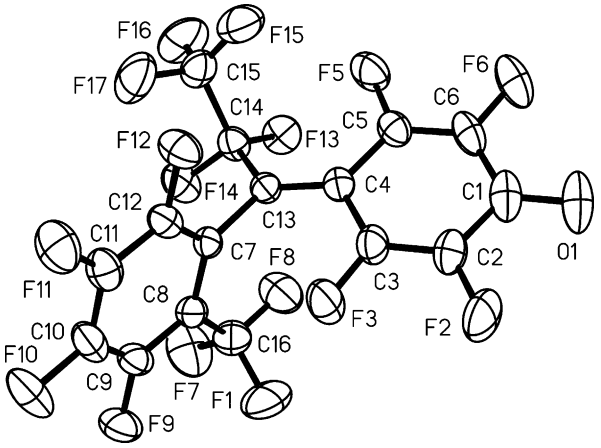


Fig. 1. Molecular structure of **2**. Thermal ellipsoids are drown at the 30% probability level. Selected bond lengths (Å) and torsion angles (°): O1–C1 1.217(4), C1–C2 1.449(5), C1–C6 1.459(5), C2–C3 1.327(4), C3–C4 1.467(4), C4–C13 1.360(3), C4–C5 1.461(4), C5–C6 1.331(4), C4–C13–C7–C12 84.1(3), C4–C13–C14–C15–90.8(3), and C3–C4–C13–C7 11.6(4).

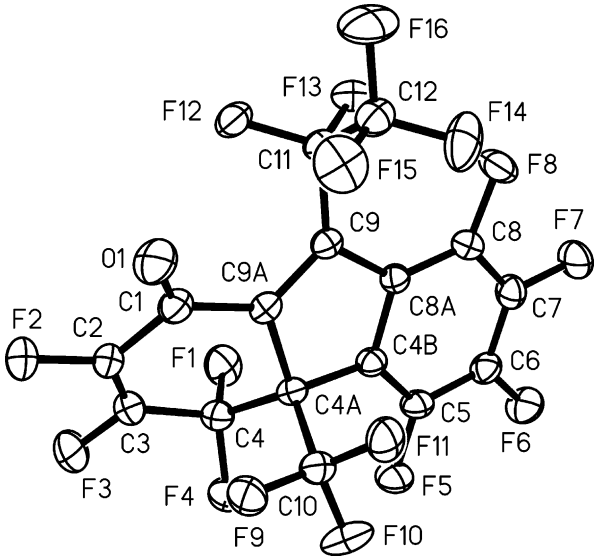


Fig. 2. Molecular structure of **4**. Thermal ellipsoids are drown at the 30% probability level. Selected bond lengths (Å) and torsion angles (°): O1–C1 1.211(5), C1–C2 1.475(6), C1–C9A 1.487(5), C2–C3 1.326(6), C3–C4 1.492(6), C4A–C9A 1.529(4), C4A–C4 1.547(5), C9–C9A 1.347(5), C3–C4–C4A–C9A −41.2(4), and C9A–C9–C11–C12 96.8(4).

In a molecule **4,** indene fragment is planar within the limits of ±0.064 Å, and the cyclohexene moiety has a sofa conformation with the C4a atom deviation of 0.571(5) Å from the plane of other atoms. In the Cambridge structural database [30] there are no structures containing a 2,3-difluoro-6-methylenecyclohex-2-enone fragment. It is necessary to note *syn*-orientation of the $C(12)F_3$ group relative to the $C(10)F_3$ group; according to gas phase DFT/PBE/TZ2P calculations *anti*-orientation is less stable by 1.5 kcal mol^{-1} than *syn*-orientation. It is interesting to note that in compound **4**, unlike compound **2**, the O1 atom has no short intermolecular contacts. Contacts F5···F14 2.830(4) and F7···F9 2.831(3) Å can be marked out.

3. Experimental

^{19}F NMR spectra were recorded on a Bruker AV 300 instrument (282.4 MHz) and on a Bruker AC 200 instrument (188.3 MHz). Chemical shifts are given in δ ppm from CCl_3F, *J* values in Hz; C_6F_6 and SO_2ClF (−162.9 and 99.9 ppm from CCl_3F) were used as internal standards. The molecular masses of the compounds were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV). GC–MS: Hewlett Packard G1081A, combined with Hewlett Packard 5890 with mass selective detector HP 5971 (EI 70 eV). Contents (yields) of products in the reaction mixtures and the purity of analytical samples (≥97%) were established by GLC and ^{19}F NMR spectroscopic data. Contents of products are given in mass percents.

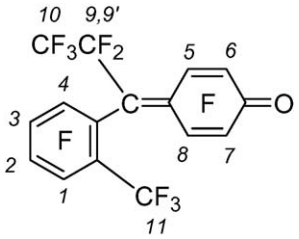
Antimony pentafluoride was distilled at atmospheric pressure (bp 142–143 °C). Benzocyclobutene **1** was obtained according to Ref. [31].

3.1. Reaction of perfluoro-1-ethyl-1-phenylbenzocyclobutene (1) with SbF_5

3.1.1. Reaction at room temperature

A mixture of benzocyclobutene **1** (0.98 g) and SbF_5 (4.94 g) (molar ratio, 1:11.5) in a sealed glass ampoule was held at 20–25 °C for 4 months. According to the ^{19}F NMR spectrum (SO_2ClF) the reaction mixture contained the salts of cations **18** and **27** (80:20). Then C_6F_6 (2 ml) was added and the mixture was poured into 5% hydrochloric acid and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent and C_6F_6 were distilled off to give 0.99 g of the product, containing 70% (yield 69%) of compound **2**, 7% (7%) of **3**, 15% (15%) of **4** and 2% (2%) of **5**. Compounds **2** (0.55 g), **4** (0.09 g) and 0.04 g of a mixture of isomers **4** and **5** (88:12) were isolated by silica gel column chromatography (CCl_4 as eluent). Ketones **2** and **4** were then sublimed (50 °C, 2 Torr). By repeated chromatography of 0.04 g of a mixture of isomers **4** and **5** (88:12) on silica gel (hexane as eluent) a fraction (0.016 g) contained isomers **4** and **5** (66:34) was isolated.

3.1.1.1. Perfluoro-4-[1-(6-methylphenyl)propylidene]cyclohexa-2,5-dienone (2).



mp 57.5–59 °C. NMR ^{19}F (282.4 MHz, $(CH_3)_2CO$): δ −55.3 (3F, CF_3-11), −77.7 (3F, CF_3-10), −99.86 (1F, F-9), −99.92 (1F, F-9′), −130.7 (1F, F-5), −132.1 (1F, F-8), −134.4 (1F, F-4), −135.9 (1F, F-1), −146.3 (1F, F-3), −146.6 (1F, F-6), −147.0 (1F, F-7), −147.3 (1F, F-2). $J_{1,2} = J_{2,3} = J_{3,4} = 21$, $J_{1,3} = 9$, $J_{1,4} = 10$, $J_{2,4} = 7$, $J_{F(1)-CF_3(11)} = 16$, $J_{F(4)-CF_3(10)} = 9$, $J_{5,6} \sim 5$, $J_{5,8} \sim J_{7,8} \sim 7$, $J_{5,9} = 54$, $J_{5,9'} = 83$, $J_{F(5)-CF_3(10)} = 29$. HRMS *m/z*, 511.9684 (M^+). Calcd for $C_{16}F_{16}O$ = 511.9688.

3.1.1.2. Perfluoro-9-ethyl-4a-methyl-4,4a-dihydrofluoren-1-one (4).

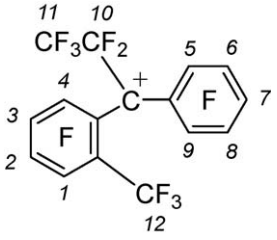
mp 71–72.5 °C. NMR ^{19}F (188.3 MHz, $CHCl_3$): δ −65.8 (3F, CF_3-4a), −83.7 (3F, $\underline{CF_3}CF_2$-9), −93.0 (1F, F_A) and −110.3 (1F, F_B, F-4), −110.7 (1F, F_{A^1}) and −111.5 (1F, F_{B^1}, $CF_3\underline{CF_2}$-9), −129.7 (1F, F-8), −132.6 (1F, F-5), −135.1 (1F, F-3), −141.4 (1F, F-2), −146.0 (1F, F-7), −146.4 (1F, F-6). $J_{A,B} = 285$, $J_{A^1,B^1} = 279$, $J_{2,3} \sim 2$, $J_{2,A} = 11$, $J_{2,B} = 15$, $J_{3,A} = 29$, $J_{3,B} = 15$, $J_{F(B)-CF_3(4a)} = 14$, $J_{F(5)-CF_3(4a)} = 19$, $J_{5,B} = 32$, $J_{5,6} = 20$, $J_{5,7} = 7$, $J_{5,8} = 15$, $J_{6,7} = 19$, $J_{6,8} = 8$, $J_{7,8} = 19$, $J_{F(8)-CF_3(9)} = 14$, $J_{8,A^1} = 67$, $J_{8,B^1} = 34$. HRMS *m/z*, 511.9688 (M^+). Calcd for $C_{16}F_{16}O$ = 511.9688.

3.1.1.3. Perfluoro-9-ethyl-4a-methyl-4,4a-dihydrofluoren-3-one (5).

Mixture with isomer **4** (**4**:**5** = 66:34). Compound **5**: NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −66.8 (3F, CF_3-4a), −84.3 (3F, $\underline{CF_3}CF_2$-9),

−105.2 (1F, F_A) and −116.2 (1F, F_B, F-4), ~−111 (2F, F-1, $CF_3\underline{CF_2}$-9), −130.2 (1F, F-8), −131.6 (1F, F-5), −141.1 (1F, F-2), −146.0 and −147.1 (2F, F-6,7). NMR ^{19}F (282.4 MHz, $CHCl_3 + (CH_3)_2CO$): δ −65.9 (3F, CF_3-4a), −83.4 (3F, $\underline{CF_3}CF_2$-9), −103.9 (1F, F_A) and −115.0 (1F, F_B, F-4), ~−110 (2F, $CF_3\underline{CF_2}$-9), −111.3 (1F, F-1), −130.4 (1F, F-8), −132.0 (1F, F-5), −140.7 (1F, F-2), −146.2 and −147.3 (2F, F-6,7). $J_{A,B}$ = 286. GC–MS *m*/*z*, 512 (M^+) for **4** and for **5**.

*3.1.1.4. Perfluoro-1-(2-methylphenyl)-1-phenylprop-1-yl cation (**18**).*



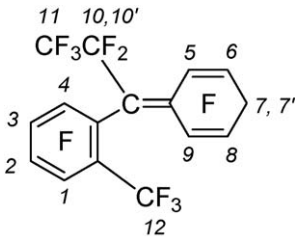
NMR ^{19}F (282.4 MHz, SbF_5–SO_2ClF): −40.5 (1F, F-7), −54.4 (3F, CF_3-12), −72.1 (1F, F-5), −74.7 (3F, CF_3-11), −83.7 (1F, F-9), −102.3 (1F, F_A) and −103.7 (1F, F_B, CF_2-10), −127.5 (1F, F-1 or F-4), −129.0 (1F, F-1 or F-4), −134.4 (1F, F-2), −140.1 (2F, F-3,8), −140.5 (1F, F-6). $J_{A,B}$ = 265, $J_{5,A}$ = 95, $J_{5,7} \sim J_{7,9} \sim$ 65, $J_{6,7} \sim J_{7,8} \sim$ 25.

3.1.2. Reaction at 50 °C

A mixture of benzocyclobutene **1** (0.92 g) and SbF_5 (2.32 g) (molar ratio, 1:5.8) in a sealed glass ampoule was heated at 50 °C for 1 month. The reaction mixture and C_6F_6 (3 ml) was placed in a Teflon container, and then anhydrous HF (7.5 ml) was added. The mixture was kept at 25 °C for 5 h, then poured onto ice and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent and C_6F_6 were distilled off to give 0.91 g of the product, containing 4% (yield 4%) of compound **2**, 52% (48%) of **6**, 12% (11%) of **7**, 14% (14%) of *E*-**8** and 8% (9%) of **9**. Compound **6** (0.21 g) and 0.15 g of a mixture of isomers **6** and **7** (75:25) were isolated by silica gel column chromatography (hexane as eluent). By repeated chromatography of 0.15 g of a mixture of isomers **6** and **7** (75:25) on silica gel (hexane as eluent) a fraction (0.03 g) contained isomers **6** and **7** (41:59) was isolated.

*3.1.2.1. Perfluoro-9-ethyl-4a-methyl-4,4a-dihydro-3H-fluorene (**6**).* Liquid NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −66.2 (3F, CF_3-4a), −84.4 (3F, $\underline{CF_3}CF_2$-9), −110.8 (1F, F_A) and −112.0 (1F, F_B, $CF_3\underline{CF_2}$-9), −111.3 (1F, F_{A^1}) and −119.2 (1F, F_{B^1}, F-4), −111.6 (1F, F_{A^2}) and −118.6 (1F, F_{B^2}, F-3), −128.2 (1F, F-1), −131.2 (1F, F-8), −132.8 (1F, F-5), −146.7 (1F, F-6), −147.4 (1F, F-2), −148.2 (1F, F-7). $J_{A,B}$ = 281, J_{A^1,B^1} = 266, J_{A^2,B^2} = 282, $J_{1,2} \sim$ 8, $J_{1,A} \sim J_{8,B} \sim$ 77, $J_{1,B} \sim J_{8,A} \sim$ 30, $J_{1,A^2} \sim J_{1,B^2} \sim$ 10, $J_{F(1)-CF_3(9)}$ = 10, $J_{2,A^2} \sim J_{2,B^2} \sim$ 23, $J_{2,B^1} \sim$ 9, $J_{F(A^2)-CF_3(4a)}$ = 15, J_{A^2,B^1} = 7, $J_{A^1,B^2} = J_{B^1,B^2}$ = 10, $J_{F(A^1)-CF_3(4a)}$ = 6, $J_{F(B^1)-CF_3(4a)}$ = 10, J_{5,B^1} = 54, $J_{F(5)-CF_3(4a)}$ = 17, $J_{5,6}$ = 20, $J_{5,7}$ = 8, $J_{5,8}$ = 15, $J_{6,7}$ = 18, $J_{6,8}$ = 7, $J_{7,8}$ = 21. HRMS *m*/*z*, 533.9706 (M^+). Calcd for $C_{16}F_{18}$ = 533.9707.

*3.1.2.2. Perfluoro-1-(1-cyclohexa-2,5-dienylidene)propyl-2-methylbenzene (**7**).*



Mixture with isomer **6** (**6**:**7** = 41:59). Compound **7**. NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −57.5 (3F, CF_3-12), −80.2 (3F, CF_3-11), −102.51 (1F, F-10), −102.55 (1F, F-10′), −109.0 (1F, F-7), −109.2 (1F, F-7′), −135.5 (1F, F-4), −136.1 (1F, F-1), −137.6 (1F, F-5), −141.0 (1F, F-9), −147.5 (1F, F-3), −148.6 (1F, F-2), −150.3 (1F, F-8), −150.6 (1F, F-6). $J_{1,2} = J_{2,3} = J_{3,4}$ = 21, $J_{1,3}$ = 8, $J_{1,4}$ = 10, $J_{F(1)-CF_3(12)}$ = 16, $J_{2,4}$ = 6, $J_{F(4)-CF_3(11)}$ = 9, $J_{5,7} \sim J_{5,7'} \sim J_{7,9} \sim J_{7',9} \sim$ 10, $J_{5,10}$ = 81, $J_{5,10'}$ = 57, $J_{F(5)-CF_3(11)}$ = 28, $J_{6,7} \sim J_{6,7'} \sim J_{7,8} \sim J_{7',8} \sim$ 22. HRMS (mixture of isomers **6**:**7** = 41:59) *m*/*z*, 533.9712 (M^+). Calcd for $C_{16}F_{18}$ = 533.9707. GC–MS *m*/*z*, 534 (M^+) for **6** and for **7**.

3.1.3. Reaction at 95 °C

A mixture of benzocyclobutene **1** (0.9 g) and SbF_5 (2.3 g) (molar ratio, 1:5.8) in a nickel bomb (10 ml) was heated at 95 °C for 72 h. Then C_6F_6 (1.5 ml) was added and the mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent and C_6F_6 were distilled off to give 0.88 g of the product, containing (GLC, ^{19}F NMR spectrum) 9% (yield 9%) of compound **3**, 15% (14%) of **4**, 2% (2%) of **5**, 5% (5%) of **6**, 7% (7%) of **8** (*E*:*Z* = 63:37), 3% (3%) of **9**, 12% (10%) of **10**, 22% (22%) of **11** (*E*:*Z* = 60:40), 11% (12%) of **12** and 3% (3%) of **13**. Compound **3** (0.064 g) and 0.1 g of a mixture, containing 61% of compound **10** and 27% of isomers **6** and **13** (60:40) were isolated by silica gel column chromatography (CCl_4 as eluent). By repeated chromatography of this mixture on silica gel (hexane as eluent) product **10** (0.02 g) and a fraction (0.011 g), containing compounds **6**, **10** and **13** (37:34:29), were isolated.

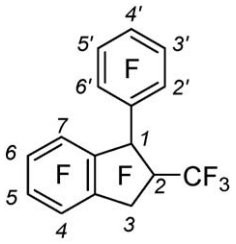
*3.1.3.1. Perfluoro-9-ethyl-9-methyl-1,2,3,4-tetrahydro-9H-fluorene (**10**).* NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −63.8 (3F, CF_3-9), −82.6 (3F, $CF_2\underline{CF_3}$), −104.6 (1F, F_A) and −105.6 (1F, F_B, $\underline{CF_2}CF_3$), −104.4, −108.8 (2F, F_{A^1}, F_{A^2}) and −120.4, −124.2 (2F, F_{B^1}, F_{B^2}, F-1,4), −123.3 (1F, F_{A^3}) and −138.9 (1F, F_{B^3}, F-2 or F-3), −124.6 (1F, F_{A^4}) and −142.8 (1F, F_{B^4}, F-3 or F-2), −128.3 (1F, F-8), −131.1 (1F, F-5), −146.3 and −146.7 (2F, F-6,7). $J_{A,B}$ = 285, $J_{A^1,B^1} \sim J_{A^2,B^2} \sim$ 280, J_{A^3,B^3} = 280, J_{A^4,B^4} = 277. HRMS *m*/*z*, 571.9682 (M^+). Calcd for $C_{16}F_{20}$ = 571.9680.

*3.1.3.2. Perfluoro-9-ethyl-4a-methyl-4,4a-dihydro-1H-fluorene (**13**).* Mixture with isomer **6** and compound **10** (**6**:**10**:**13** = 37:34:29). GC–MS *m*/*z*, 534 (M^+) for **6** and for **13**; 572 (M^+) for **10**. Compound **13**: NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −65.9 (3F, CF_3-4a), −82.2 (3F, $CF_2\underline{CF_3}$), −92.4 (1F, F_A) and −101.3 (1F, F_B, F-1), −94.5 (1F, F_{A^1}) and −112.6 (1F, F_{B^1}, F-4), −106.6 (1F, F_{A^2}) and −108.1 (1F, F_{B^2}, $\underline{CF_2}CF_3$), −130.3 (1F, F-8), −132.0 (1F, F-5), −146.2 and −147.3 (2F, F-6,7), −149.0 and −150.3 (2F, F-2,3). $J_{A,B}$ = 300, J_{A^1,B^1} = 282, J_{A^2,B^2} = 283.

*3.2. Reaction of perfluoro-2-methylindan (**25**) with C_6F_5H in the presence of SbF_5*

A mixture of indan **25** and SbF_5 was prepared by heating of perfluoro-1-ethylbenzocyclobutene (1.7 g, 4.89 mmol) with SbF_5 (5.95 g, 27.44 mmol) in a nickel bomb (10 ml) at 130 °C for 12 h [3]. Then pentafluorobenzene (0.95 g, 5.65 mmol) and C_6F_6 (3 ml) were added to the mixture. The resulting mixture was held at 25 °C for 48 h, then poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent and C_6F_6 were distilled off to give 2.2 g of the product, containing 11% of compound **8** (*E*:*Z* = 50:50), 66% of **11** (*E*:*Z* = 57:43) and 5% of **24**. By silica gel column chromatography (CCl_4, then $CHCl_3$ as eluents) there were isolated compounds **8** (0.2 g, *E*:*Z* = 50:50), **24** (0.03 g) and **11** (0.06 g, *E*:*Z* = 20:80; 0.9 g, *E*:*Z* = 54:46; 0.05 g, *E*:*Z* = 88:12). By repeated chromatography of 0.2 g of the mixture of isomers **8** (*E*:*Z* = 50:50) on silica gel (hexane as eluent) there were isolated fractions, containing compound **8** with a predominance of one or another isomer (0.04 g, *E*:*Z* = 80:20; 0.012 g, *E*:*Z* = 18:82).

*3.2.1. Perfluoro-2-methyl-1-phenylindan (**8**)*



mixture of *E*- and *Z*-isomers (*E*:*Z* = 80:20, *E*:*Z* = 18:82).

3.2.1.1. E-isomer. NMR ^{19}F (282.4 MHz, $CHCl_3$): δ–73.2 (3F, CF_3), −96.4 (1F, F_A) and −104.3 (1F, F_B, F-3), −137.2 (1F, F-2′), −138.6 (1F, F-6′), −139.2 (1F, F-4), −140.2 (1F, F-7), −143.8 (1F, F-6), −144.5 (1F, F-5), −146.3 (1F, F-1), −148.3 (1F, F-4′), −159.8 and −161.2 (2F, F-3′,5′), −174.1 (1F, F-2). $J_{A,B}$ = 273, $J_{1,2'}$ ∼70, $J_{F(1)-CF_3}$ ∼ 19, $J_{1,5}$ = 7, $J_{F(A)-CF_3}$ ∼ 16, $J_{4,5}$ = 20, $J_{4,6}$ = 6, $J_{4,7}$ = 17, $J_{5,6}$ = 20, $J_{5,7}$ = 7, $J_{6,7}$ = 21, $J_{2',3'} \sim J_{3',4'} \sim J_{4',5'} \sim J_{5',6'} \sim 22$, $J_{2',4'} \sim J_{4',6'} \sim 5$, $J_{3',5'} \sim 7$.

3.2.1.2. Z-isomer. NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −74.3 (3F, CF_3), −100.0 (2F, F-3), −135.0 (1F, F-2′), −139.3 (1F, F-6′), −139.5 (1F, F-4), −139.9 (1F, F-7), −143.7 (1F, F-6), −144.7 (1F, F-5), −145.5 (1F, F-1), −148.0 (1F, F-4′), −159.3 and −160.9 (2F, F-3′,5′), −177.5 (1F, F-2). $J_{1,2'}$ = 72, $J_{1,5}$ = 6, $J_{4,5} = J_{5,6} = J_{6,7}$ = 20, $J_{4,6} = J_{5,7}$ = 7, $J_{4,7}$ = 17, $J_{2',3'} \sim J_{3',4'} \sim J_{4',5'} \sim J_{5',6'} \sim 22$, $J_{2',4'} \sim J_{4',6'} \sim 5$, $J_{3',5'} \sim 7$. HRMS (*E*:*Z* = 50:50) *m*/*z*, 495.9744 (M^+). Calcd for $C_{16}F_{16}$ = 495.9744. GC–MS *m*/*z*, 496 (M^+) for *E*-**8** and for *Z*-**8**.

*3.2.2. 1-Hydroxyperfluoro-2-methyl-1-phenylindan (**11**)*

Mixture of *E*- and *Z*-isomers (*E*:*Z* = 88:12, *E*:*Z* = 20:80).

3.2.2.1. E-isomer. NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −72.4 (3F, CF_3), −94.4 (1F, F_A) and −107.0 (1F, F_B, F-3), −136.6 and −141.3 (2F, F-2′,6′), −140.5 (1F, F-4), −142.4 (1F, F-7), −145.5 (1F, F-6), −148.5 (1F, F-5), −150.4 (1F, F-4′), −161.0 and −161.4 (2F, F-3′,5′), −171.4 (1F, F-2). $J_{A,B}$ = 271, $J_{F(2)-CF_3}$ = 7, $J_{F(A)-CF_3}$ = 15, $J_{4,5}$ = 21, $J_{4,6}$ = 7, $J_{4,7}$ = 17, $J_{5,6}$ = 19, $J_{5,7}$ = 6, $J_{6,7}$ = 21, $J_{2',4'} \sim J_{4',6'} \sim 5$, $J_{3',4'} \sim J_{4',5'} \sim 22$.

3.2.2.2. Z-isomer. NMR ^{19}F (282.4 MHz, $CHCl_3$): δ–73.9 (3F, CF_3), −99.3 (1F, F_A) and −100.1 (1F, F_B, F-3), −137.1 and −138.9 (2F, F-2′,6′), −141.0 (1F, F-4), −141.4 (1F, F-7), −145.2 (1F, F-6), −148.2 (1F, F-5), −150.3 (1F, F-4′), −160.5 and −161.3 (2F, F-3′,5′), −175.8 (1F, F-2). $J_{A,B}$ = 273, $J_{4,5}$ = 20, $J_{4,6}$ = 7, $J_{4,7}$ = 17, $J_{5,6} = J_{6,7}$ = 19, $J_{5,7}$ = 6, $J_{2',3'} \sim J_{3',4'} \sim J_{4',5'} \sim J_{5',6'} \sim 22$, $J_{2',4'} \sim J_{4',6'} \sim 5$, $J_{3',5'} \sim 7$. HRMS (*E*:*Z* = 88:12) *m*/*z*, 493.9785 (M^+), (*E*:*Z* = 20:80) *m*/*z*, 493.9784 (M^+). Calcd for $C_{16}F_{16}$ = 495.9744.

*3.2.3. Perfluoro-8-methyl-7-phenylbicyclo[4.3.0]nona-1,4,6-trien-3-one (**24**)*

NMR ^{19}F (282.4 MHz, $CHCl_3$): δ −75.8 (3F, CF_3), −105.9 (1F, F_A) and −110.4 (1F, F_B, F-6), −122.5 (1F, F-4), −135.5 (1F, F-2′), −137.0 (1F, F-1), −138.6 (1F, F-6′), −138.9 (1F, F-2), −147.0 (1F, F-4′), −159.8 and −160.0 (2F, F-3′,5′), −168.2 (1F, F-7). $J_{A,B}$ = 277, $J_{1,2}$ = 9, $J_{1,2'} \sim J_{1,6'} \sim 7$, $J_{2,4}$ = 7, $J_{4,A}$ = 7, $J_{4,B}$ = 8, $J_{F(B)-CF_3}$ = 17, $J_{F(7)-CF_3}$ = 12, $J_{7,2'} \sim 36$. HRMS *m*/*z*, 473.9730 (M^+). Calcd for $C_{16}F_{14}O$ = 473.9725.

*3.3. Perfluoro-2-methyl-1-phenylindan-1-yl cation (**19**)*

Indan **8** (0.07 g) was dissolved in SbF_5 (1.22 g) (molar ratio, 1:40), then SO_2ClF (0.1 g) was added at 0 °C and NMR ^{19}F spectrum of the solution was measured at 20 °C. The spectrum contained the signals of cation **19** in the absence of the signals of the precursor **8**. The solution was poured into water and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$, and CH_2Cl_2 was distilled off to give 0.065 g of the product, containing 10% of compound **8** (*E*:*Z* = 67:33), 60% of **11** (*E*:*Z* = 38:62) and 22% of **24**.

*3.3.1. Cation (**19**)*

NMR ^{19}F (282.4 MHz, SbF_5–SO_2ClF): δ −66.8 (3F, CF_3), ∼−88 (2F, F-4′,5), −91.8 (1F, F_A) and −102.8 (1F, F_B, F-3), −96.6 (1F, F-2′), −99.9 (1F, F-6′), −111.0 (1F, F-7), −127.6 (1F, F-4), −133.0 (1F, F-6), −148.0 (2F, F-3′,5′), −163.1 (1F, F-2). $J_{A,B}$ = 255, $J_{2',2}$ = 67.

*3.4. Perfluoro-1-methyl-2-phenylindenyl cation (**23**)*

An analogous procedure was used to generate cation **23** from indene **9** (0.06 g) and SbF_5 (1.14 g) (molar ratio, 1:40) in SO_2ClF (0.21 g). Hydrolysis of the salt of cation **23** yielded 0.055 g of the product, containing (GLC, ^{19}F NMR spectrum) 95% of compound **12**.

*3.4.1. Cation (**23**)*

NMR ^{19}F (282.4 MHz, SbF_5–SO_2ClF): δ 18.3 (1F, F-1), −57.9 (1F, F-7), −67.7 (3F, CF_3), −89.3 (1F, F-4 or F-5), −91.0 (1F, F-4 or F-5), −131.7 (2F, F-2′,6′), −137.8 (1F, F-6 or F-4′), −142.2 (1F, F-6 or F-4′), −157.4 (2F, F-3′,5′). $J_{1,4} \sim J_{5,7} \sim 55$, $J_{1,7} \sim 90$.

*3.5. Perfluoro-9-ethyl-4a-methyl-4,4a-dihydro-3H-fluoren-3-yl cation (**27**)*

Cation (**27**) was generated by the analogous procedure from compound **6** (0.085 g) and SbF_5 (1.29 g) (molar ratio, 1:37) in SO_2ClF (0.17 g). Hydrolysis of the salt of cation **27** yielded 0.05 g of the product, containing 75% of compound **4**, 12% of **5**, 4% of **6** and 2% of **13**.

*3.5.1. Cation (**27**)*

NMR ^{19}F (282.4 MHz, SbF_5–SO_2ClF): δ −17.7 (1F, F-1), −64.1 (3F, CF_3-4a), −69.5 (1F, F-3), −79.5 (3F, $CF_2\underline{CF_3}$), −85.6 (1F, F_A) and −112.6 (1F, F_B, F-4), −94.1 (1F, F-8), −98.2 (1F, F-6), −105.0 (1F, F_{A^1}) and −106.1 (1F, F_{B^1}, $\underline{CF_2}CF_3$), 41.5 (1F, F-5), ∼29.3 (2F, F-2,7). $J_{A,B}$ = 301, J_{A^1,B^1} = 287.

3.6. X-ray crystallography

A powder of compound **2** or **4** was placed in an ampoule. Then the ampoule was evacuated (2 Torr), sealed and heated at 50 °C during 2 weeks. Single crystals of compounds **2** and **4** were grown.

The X-ray diffraction experiments were carried out on a Bruker P4 diffractometer (graphite monochromated Mo Kα radiation, θ/2θ-scan, $2\theta < 54°$) at room temperature. Reflection intensities of **2** and **4** were corrected for evaporation and absorption (**2**) by empirical method. The structures were solved by direct methods and refined by anisotropic full-matrix least squares against F^2 of all reflections using SHELX-97 programs [32]. Crystallographic data for the structures **2** and **4** in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplement publication no. CCDC 698633 and 698634. Copy of the data can be obtained, free of charge, on application to CCDC (e-mail: deposit@ccdc.cam.ac.uk, internet: http://www.ccdc.cam.ac.uk/deposit).

3.6.1. Crystallographic data and refinement parameters for 2

$C_{16}F_{16}O$, *M* = 512.16, orthorhombic, space group *Pbca*, *a* = 9.9571(15), *b* = 18.010(2), *c* = 19.140(2) Å, *V* = 3432.3(8), *Z* = 8, D_{calc} = 1.982 g cm^{-3}, μ = 0.243, 6412 total reflexions, 3751 unique reflexions (R_{int} = 0.1066), *R* = 0.0477 for 2142 $I > 2\sigma(I)$, 298 parameters, wR_2 = 0.1533 and GOF = 1.022 for all data, max/min Δρ 0.28/−0.23.

3.6.2. Crystallographic data and refinement parameters for **4**

$C_{16}F_{16}O$, M = 512.16, monoclinic, space group *Cc*, a = 9.3786(5), b = 16.2874(9), c = 10.7469(6) Å, V = 1641.4(2), Z = 4, D_{calc} = 2.073 g cm^{-3}, μ = 0.254, 1893 total unique reflexions, R = 0.0286 for 1531 $I > 2\sigma(I)$, 298 parameters, $wR_2 = 0.0843$ and GOF = 1.091 for all data, max/min $\Delta\rho$ 0.19/−0.19.

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