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Stable *gem*-trifluoromethyl anionic σ-complexes based on 1,3,5-tris(sulfonyl)benzene derivatives and their transformations

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ABSTRACT

A convenient synthetic procedures is described to obtain gem-trifluoromethyl anionic σ-complexes of 1,3,5-tris(fluorosulfonyl)benzene, 1,3,5-tris(β,β,β-trifluoroethoxysulfonyl)benzene, 1,3,5-tris(trifluoromethylsulfonyl)benzene as well as of 1,3,5-trinotrobenzene. Conditions for easy oxidation of these adducts into corresponding 2,4,6-tris(substituted)benzotrifluorides have been found. It is shown that the latter add trifluoromethyl anion to the 1 and 3 positions of the aromatic ring forming new anionic σ-complexes in different ratio. Structures and relative stabilities of the anionic adducts are discussed based on RI-MP2 quantum chemical calculations.

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1. Introduction

As a matter of fact anionic σ-complexes of the Meisenheimer type are steel of grate interest as intermediates in the reactions of aromatic nucleophilic substitution. Their grate importance is caused by the possibility of further transformation into the final novel products in many ways [1]. The chemistry of anionic σ-complexes is widely investigated for the aromatic compounds with strong electron withdrawing groups. In particular, the reactions of 1,3,5-trinitrobenzene [2] and 1,3,5-tris(trifluoromethylsulfonyl)-benzene [2f,2i, 3] with different C-nucleophiles are well documented in literature. Most of these adducts were isolated and successfully oxidized into the corresponding 1,2,4,6-tetrasubstituted benzenes [2,3].

We focus our attention on the σ-complexes with CF_3 group at the sp^3-carbon atom. These adducts attract our interest because trifluoromethyl-containing aromatic molecules are known to be valuable starting material in preparing new drugs and other biologically active compounds [4].

However, up to now there are only few examples in literature for the synthesis and study of further transformations of the σ-complexes with the extremely unstable perfluoroakyl anions. In particular, CF_3-containing anionic σ-complex of 1,3,5-trinitrobenzene was detected by ^1H NMR spectroscopy in the reaction mixture. Trifluoromethyl ion was generated *in situ* by the termolysis of potassium trifluoroacetate [2h]. Noteworthy, the practical application of this method is rather limited, due to the high reaction temperature (>150 °C), which can cause partial decomposition of the initial substrates and the formed anionic σ-complexes.

The modern method to generate [CF_3^-] is deal with using a very popular and easily available Ruppert reagent, Me_3SiCF_3/F^- [5]. Thus the formation of trifluoromethyl-containing anionic σ-complexes was postulated in the reactions of some nitroarenes with Me_3SiCF_3 in the presence of fluoride ion. The subsequent oxidation of these adducts led to the formation of a mixture of isomeric trifluoromethyl-containing benzene derivatives [2l]. Also using the Me_3SiCF_3/TASF system in the reaction with 1,2,4,5-tetrakis(trifluoromethyl)benzene enabled preparing under mild conditions a stable anionic σ-complex containing two trifluoromethyl groups at the geminal center [6].

Our scientific group is interested in aromatic compounds activated by very strong electron-withdrawing substituents, SO_2F and SO_2CF_3. Recently we have developed a suitable method for preparation of 1,3,5-tris(fluorosulfonyl)benzene and its derivatives [7,8]. It is pertinent to remark here that to best of our knowledge in the literature there are no examples of organic molecules containing both CF_3 and above mentioned groups. That is why it seems to us interesting and important to check the possibility of their formation.

In the present paper we report our systematic investigation on the reactions of the 1,3,5-tris(trifluoromethylsulfonyl)benzene **1**,

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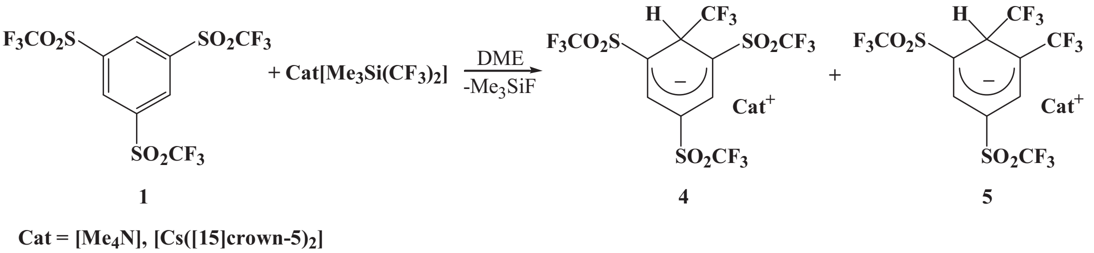


Scheme 1.

1,3,5-tris(fluorosulfonyl)benzene **2** and 1,3,5-tris(β,β,β-trifluoroethoxysulfonyl)benzene **3** with the Me_3SiCF_3/F^-system, aimed on preparing of new trifluoromethyl-containing anionic σ-complexes and studying on their transformation to the corresponding novel aromatic products.

2. Results and discussion

At the beginning it should be noted that among above mentioned 1,3,5-tris(sulfonyl)benzene derivatives **1**–**3**, the reactions of complex formation were widely investigated only for 1,3,5-tris(trifluoromethylsulfonyl)benzene **1**. In particular, the interaction between substrate **1** and a number of non-fluorinated organosilicon compounds (Me_3SiCH_2COOMe, $Me_3SiC(O)Me$, $PhCH_2SiMe_3SiCH_2Ph$, etc.) in the presence of fluoride ion in THF at 25 °C was substantially explored [2f]. Surprisingly it was found that sulfon **1** does not demonstrate the C–C bond formation under these reaction conditions. An adduct with fluoride ion was postulated as the only product.

Our idea was to test the possibility of CF_3-containing complex formation by the reaction between compound **1** and Me_3SiCF_3/F^- system.

We have found that sulfone **1** interacts with Me_3SiCF_3 at -60 ± 5 °C in the presence of tetramethylammonium fluoride forming anionic σ-complex **4**. Unfortunately the yield of adduct **4** was very low under these reaction conditions. According to ^{19}F NMR spectra CF_3H and Me_3SiF, the products of Me_3SiCF_3 transformations were the main products in the reaction mixture. Using other fluoride ion sources, such as potassium and cesium fluorides in combination with crown ethers, as well as increasing of the reaction temperature does not improve the result.

Me_3SiCF_3 is known to react with fluoride ion to form pentacoordinated silicon complex $Cat[Me_3Si(CF_3)_2]$, which is a convenient source of trifluoromethyl anion excluding the presence of F^- [13]. Our experiments have shown that in contrast to the above mentioned Me_3SiCF_3/Me_4NF system, the generated *in situ* silicate $[Me_4N][Me_3Si(CF_3)_2]$ reacts with sulfone **1** in DME at -60 ± 5 °C smoothly forming a mixture of anionic σ-complexes **4** and **5** in ratio 4:1 (Scheme 1).

Probably, along with the reaction at the free position of the aromatic ring, the ipso-attack of the $[CF_3^-]$ intermediate takes place followed by elimination of SO_2CF_3 group and forming **5**. A similar nucleophilic substitution of SO_2CF_3 group was previously reported in the reactions of the sulfone **1** with S-nucleophiles [3b]. A conversion of the initial substrate does not exceed 60%, probably due to the low solubility of **1** under the reaction conditions. Increasing the reaction temperature is however not possible, because the silicate $[Me_4N][Me_3Si(CF_3)_2]$ is unstable at temperatures above −55 °C. In order to increase a conversion degree of **1** the silicate $[Cs([15]crown\text{-}5)_2][Me_3Si(CF_3)_2]$ [14] was synthesized that is stable in the solution up to −5 °C. In the reaction of **1** with this silicate in DME in temperature range from −50 °C to −15 °C,

Table 1

^1H and ^{19}F NMR data of the anionic σ-complexes **4**–**6**, **8**, **10**, **14**–**19** (DMSO-d_6), (δ/ppm, J/Hz). The numbering of the C-atoms see in Scheme 6.

Compound	$^1H^*$		^{19}F	
	1-H	3,5-H	CF_3	R
4	4.68 (q, $^3J_{H,F} = 7.5$)	7.87 (s)	-78.31^a (d, $^3J_{F,H} = 7.5$)	-81.43^b (s); -81.8^c, (s)
5	4.45 (q, $^3J_{H,F} = 6.9$)	7.80 (s) 7.22 (s)	-77.28^a (m); -63.12^d (q, $^5J_{F,F} = 5.6$)	−81.87 (s); −81.84 (s)
6	5.36 (q, $^3J_{H,F} = 7.7$)	8.27 (s)	-77.57^a, tm, ($^5J_{F,F} = 9.5$)	67.5^b (qd, $^5J_{F,F} = 9.5$; $^4J_{F,H} = 1.7$); 68.7^c (s)
8[f]	4.92 (q, $^2J_{H,F} = 7.7$)	7.80 (s)	-76.60^a (d, $^3J_{F,H} = 7.7$)	-75.69^b (t, $^3J_{F,H} = 9$); -75.89^c (t, $^3J_{F,H} = 9$)
10	5.8 (q, $3J_{H,F} = 6.3$)	8.49 (s)	-71.39^a (d, $^3J_{F,H} = 6.3$)	
14		8.34 (s)	-66.70^a (m)	66.57^b (q, $^5J_{F,F} = 12$); 68.6^c (s)
15	5.34 (q, $^3J_{H,F} = 9$)	8.14 (s)	-77.71^a (t, $^5J_{F,F} = 12$); -54.4^e (t, $^5J_{F,F} = 12$)	63.49 (q, $^5J_{F,F} = 12$); 66.98 (q, $^5J_{F,F} = 12$) 69.14 (q, $^5J_{F,F} = 12$)
16[f]		7.95 (s)	-66.80^a (m)	−75.21 (m); −75.52 (m)
17[f]	5.03 (q, $^3J_{H,F} = 8.8$)	7.65 (s)	-75.95^a (d, $^3J_{F,H} = 8.8$); -53.5^e (s)	−73.63 (m); −74.03 (m)
18		8.72 (s)	−65.04 (m)	
19	5.84 (q, $^3J_{H,F} = 8.8$)	8.47 (s)	-74.66^a (d, $^3J_{F,H} = 8.8$); -53.5^e (s)	

[a] CF_3 in position 1.
[b] 2,6-R.
[c] 4-R.
[d] CF_3 in position 2.
[e] CF_3 in position 3.
[f] δH CH_2 for compound **8**: 4.6 (q, $^3J_{H,F} = 9$ Hz, 2H, o-$SO_3CH_2CF_3$), 4.53 (q, $^3J_{H,F} = 9$ Hz, 2H, o-$SO_3CH_2CF_3$), 4.42 (q, $^3J_{H,F} = 9$ Hz, 2H, p-$SO_3CH_2CF_3$); for compound **16**: 4.62 (q, J = 8.2 Hz, 4H, o-$SO_3CH_2CF_3$), 4.53 (q, J = 8.2 Hz, 2H, p-$SO_3CH_2CF_3$); for compound **17**: 4.60 (q, J = 8.2 Hz, 4H, o-$SO_3CH_2CF_3$), 4.51 (q, J = 8.2 Hz, 2H, p-$SO_3CH_2CF_3$.
[*] δH $(CH_3)_4N$ for compounds **4**–**6**, **8**, **10**, **14**–**19**: 3.31 (12H, CH_3).

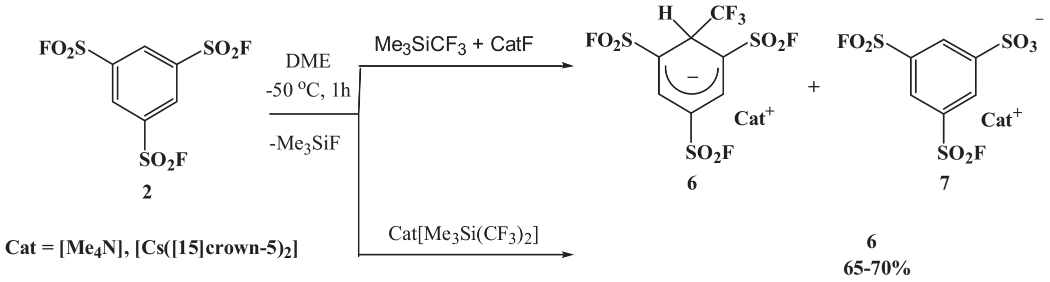
Table 2
^{13}C NMR data of the anionic σ-complexes **6**, **8**, **10**, **14–16** (THF-d_8), (δ/ppm, *J*/Hz). The numbering of the C-atoms see in Scheme 6.

Compound	1-C	2,6-C	3,5-C	4-C	CF$_3$
6	41.03 (q, $^2J_{C,F}=33$)	95.62 (d, $^2J_{C,F}=27$)	142.29 (s)	98.33 (q, $^2J_{C,F}=27$)	126.48[a] (q, $^1J_{C,F}=288$)
8[c]	41.79 (q, $^2J_{C,F}=32$)	94.39 (s)	140.93 (s)	98.66 (s)	127.12[a](q, $^1J_{C,F}=290$)
10	42.74 (q, $^2J_{C,F}=31$)	125.18 (s)	130.18 (s)	122.94 (s)	126,6[a] (q, $^1J_{C,F}=288$)
14		89.82 (d, $^2J_{C,F}=31$)	145.48 (s)	101.49 (d, $^2J_{C,F}=31$)	123.57[a] (q, $^1J_{C,F}=290$)
15	42.43 (q, $^2J_{C,F}=33$)	95.57 (d, $^2J_{C,F}=28$)	139.65 (q, $^2J_{C,F}=35$, 3-C) 142.09 (s, 5-C)	99.51 (d, $^2J_{C,F}=28$)	123.7[a] (q, $^1J_{C,F}=288$) 125.89 [b] (q, $^1J_{C,F}=285$)
16[c]	59.51 (q, $^2J_{C,F}=31$)	97.77 (s)	143.47 (s)	94.68 (s)	122.54[a] (sep, $^1J_{C,F}=290$)

[a] CF$_3$ in position 1.

[b] CF$_3$ in position 3.

[c] δC (OCH$_2$CF$_3$) for compound **8** 124.28 (q, $^1J_{C,F}=277$, *o*-OCH$_2$CF$_3$), 64.99 (q, $^2J_{C,F}=37$, *o*-OCH$_2$CF$_3$); 124.38 (q, $^1J_{C,F}=277$, *p*-OCH$_2$CF$_3$), 64.61 (q, $^2J_{C,F}=37$, *p*-OCH$_2$CF$_3$); for compound **16** 122.41 (q, $^1J_{C,F}=278$, *o*-OCH$_2$CF$_3$); 63.57 (q, $^2J_{C,F}=37$, *o*-OCH$_2$CF$_3$); 122.55 (q, $^1J_{C,F}=278$, *p*-OCH$_2$CF$_3$) 63.15 (q, $^2J_{C,F}=37$, *p*-OCH$_2$CF$_3$).



Scheme 2.

the conversion of the starting compound increases from 60 to 95% and the total yield of the anionic complexes **4** and **5** with the same ratio (4:1) has been brought to 65%.

Unfortunately, the complexes **4** and **5** have been not separated therefore they are characterized in mixture by ^{1}H, ^{19}F NMR spectra (Tables 1 and 2).

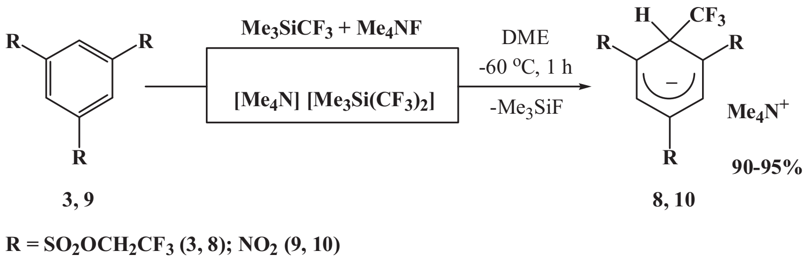
We next examined the reactivity of 1,3,5-tris(fluorosulfonyl)-benzene **2** in the context of the CF$_3$-containing σ-complex formation. Fluorosulfonyl group is very similar by its electronic properties ($\sigma_p = 1.01$ [9]) to the trifluoromethylsulfonyl substituent ($\sigma_p = 1.04$ [9]), thus it can be supposed that compound **2** is activated enough to form anionic σ-complex and recently we have provided experimental evidence for this fact [10]. It is pertinent to remark here that sulfonylfluoride **2** presents interesting possibilities in the sense that it has two potential electrophilic centers for reaction with nucleophile – SO$_2$F group and a free position of the aromatic ring.

Continue our investigations we have found that **2** reacts with Me$_3$SiCF$_3$ in the presence of fluoride ion in DME at -50 ± 5 °C forming anionic σ-complex **6** (~45 mol.%) and 3,5-bis(fluorosulfonyl)benzenesulfonate **7** as a by-product (Scheme 2). The overall conversion of the substrate under these conditions does not exceed 80%.

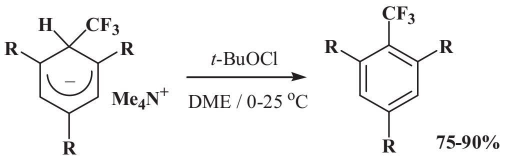
We consider that product **7** is a result of hydrolyses of SO$_2$F group caused by the presence of fluoride ion in the reaction mixture. Because on the one hand [Me$_4$N]F, for example, is a strong base and on the other hand F$^-$ is known to interact with glass producing some moisture. To confirm our assumption the reaction of **2** with CatF was carried out to produce sulfonate **7**. Also it should be noted that the same product was obtained as a result of interaction between substrate **2** and KHCO$_3$ in DMSO. Its structure was proved by ^{1}H, ^{19}F и ^{13}C NMR spectral data.

In order to decrease the yield of the co-product, the reactions of the sulfonyl fluoride **2** with several trifluoromethylsilicates have been investigated. Thus, **2** reacts with the generated *in situ* silicates Cat[Me$_3$Si(CF$_3$)$_2$] in DME at -50 ± 5 °C forming the stable anionic σ-complex **6** in 65–70% yield (Scheme 2). The conversion of the substrate **2** in the reaction with the silicates is 100% and the by-product **7** is not formed. However, the formation of another unidentified species (about 10–15 mol. %) alongside with the main product **6** has been detected by ^{19}F NMR spectrum. Unfortunately we failed to isolate pure anionic σ-complex **6** and it was characterized only in the mixture by means of ^{1}H, ^{19}F and ^{13}C NMR spectra (Tables 1 and 2).

The next object of our investigation, 1,3,5-tris(β,β,β-trifluoroethoxysulfonyl)benzene **3** was obtained in our laboratory during the course of investigation of the sulfonyl center reactivity in compound **2** [12]. It should be noted that SO$_2$OCH$_2$CF$_3$ group is a rather electron withdrawing substituent (σ_p-SO$_2$OCH$_2$CF$_3$ = 0.88 [11]). Furthermore, in contrast to the compounds containing non-fluorinated alkoxysulfonyl groups, which are strong alkylating agents, the derivatives including SO$_2$OCH$_2$CF$_3$ groups are stable



Scheme 3.



6, 8, 10 **11-13**

R=SO_2F (6, 11); $SO_2OCH_2CF_3$ (8, 12); NO_2 (10, 13)

Scheme 4.

and exhibit significantly lower alkylating properties [11]. From the above it can be seen that compound **3** presents interesting possibilities as a substrate for anionic σ-complex formation.

We have found that in contrast to the sulfone **1** and sulfonyl fluoride **2**, sulfonyl ester **3** reacts selectively both with Me_3SiCF_3 in the presence of fluoride ion and with the silicates Cat[$Me_3Si(CF_3)_2$] in DME at -50 ± 5 °C producing the stable trifluoromethyl-containing anionic σ-complex **8** in quantitative yield (Scheme 3).

Taking into account that trifluoromethyl-containing σ-complex of 1,3,5-trinitrobenzene **9** was not isolated as individual compound we examined the complexation reaction of TNB with Me_3SiCF_3/F^- in DME at −60 °C.

It has been found that under these reaction conditions stable anionic σ-complex **10** is formed with quantitative yield (Scheme 3).

Anion **8** has been isolated as yellow solid with mp 71–72 °C, whereas **10** is a dark-red solid with mp 170 °C. The structures of **8** and **10** agree with the data of elemental analysis and ^1H, ^{19}F, ^{13}C NMR spectra (Tables 1 and 2).

Anionic σ-complexes **6**, **8** and **10** have been further oxidized to 2,4,6-trisubstituted benzotrifluorides **11**–**13**. The oxidation has been carried out using *t*-BuOCl in DME in temperature range 0–25 °C and usually was completed within a few minutes (Scheme 4).

Although the anionic σ-complex **6** has not been isolated in the pure form, we had a success to obtain 2,4,6-tris(fluorosulfonyl)-benzotrifluoride **11** in 75% yield by the oxidation of the mixture of **6** with the co-product and subsequent purification.

The oxidation of the compounds **8** and **10** proceeds with high yields with the formation of 2,4,6-tris(β,β,β-trifluoroethoxysulfonyl)benzotrifluoride **12** and 2,4,6-trinitrobenzotrifluoride **13**, respectively. It should be noted that the yield of product **13** in the proposed reaction (85%) is higher compared to those reported previously (33% [2l] and 40% [2h]) and hence this method can be used for a suitable preparative synthesis of **13**.

Unfortunately, numerous attempts to carry out the oxidation of complexes **4** and **5** have been resulted in inseparable and unidentifiable product mixtures.

The prepared 2,4,6-trisubstituted benzotrifluorides **11**–**13** are more electrophilic than the starting 1,3,5-trisubstituted benzenes **2**, **3** and **9**, due to the presence of an additional electron withdrawing CF_3 group, and can be also expected to form stable anionic σ-complexes. In the reactions with Me_3SiCF_3 in the presence of Me_4NF as well as with silicate [Me_4N][$Me_3Si(CF_3)_2$] they undergo the nucleophilic addition of the [CF_3^-] both at position 1 and 3 of the aromatic ring producing the corresponding isomeric anionic σ-complexes **14**–**19** (Scheme 5).

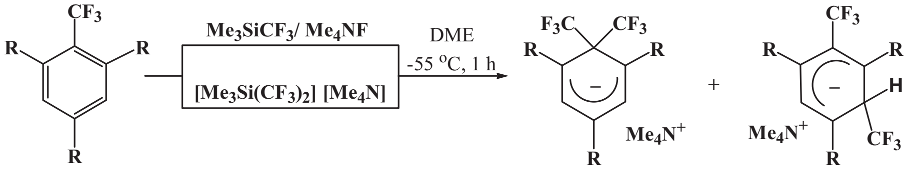
The reaction of **11** with silicate [Me_4N][$Me_3Si(CF_3)_2$] yields a mixture of **14** and **15** in ratio 1:2 with the total yield 85%. Compound **12** interacts with the Me_3SiCF_3/F^- system and undergoes CF_3-addition mainly at the first position of the aromatic ring forming the anionic complex **16** as a major product. In contrast, trinitrobenzotrifluoride **13** forms predominantly the anionic σ-complex **19** with addition of the trifluoromethyl anion mainly at the third position of the aromatic ring.

The adduct **16** is stable and has been isolated in pure form as a yellow solid with mp 109–110 °C. Complexes **14** and **15** are also stable but unfortunately we were not able to separate them. At the same time the trinitro-derivatives **18** and **19** are unstable and can be detected only in the reaction mixture by means of the ^{19}F and ^1H NMR spectra (Table 1).

3. Quantum chemical investigation of anionic σ-complexes

The structures of all the anionic σ-complexes, as well as the corresponding starting aromatic compounds have been fully optimized at the DFT and RI-MP2 levels of theory. There are special peculiarities inherent to all investigated anion structures are deviations from planarity of the ring and H-bounding of all hydrogens to oxygen atoms. Additionally, in all anion structures the C2–C3 (C5–C6) bonds are shorter (1.36–1.39 Å) than the C3–C4 and C4–C5 ones (1.41–1.42 Å) and these in turn are shorter than the bonds at the formally sp^3-hybridized C1 atom, C1–C2 and C1–C6 (1.49–1.50 Å), hence most correct representation of the anion structures best agrees with the mesomeric form shown in Scheme 6.

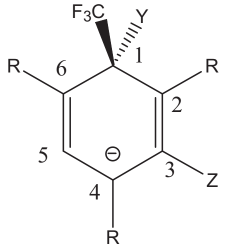
RI-MP2 energy optimization predicts for anion **10** Cs symmetrical structure shown in Fig. 1. The six-membered ring in **10** indicates a slight boat-type distortion from the planar conformation. Four carbon atoms (C2, C3, C5 and C6) form a plane whereas C1 and C4 are out of plane, the former deviates more (∠C1C2C3C5 = 17.7°) than the latter (∠C4C3C2C6 = −8.1°). An *equatorial* position of the C1–H hydrogen is favored by forming hydrogen bonds with oxygens of the *ortho*-NO_2 substituents. The CF_3 group is *axial*, diminishing an unfavorable closeness of the latter to the NO_2 moieties. Similar to **10**, a structure of the unsymmetrical CF_3-disubstituted σ-complex **19** is boat-like distorted, too (∠C1C2C3C5 = −17.1°, ∠C1C6C5C3 = 21.9°,



11-13 **14, 16, 18** **15, 17, 19**

R = SO_2F (11, 14, 15)	**1**	**:**	**2**
R = $SO_2OCH_2CF_3$ (12, 16, 17)	**9**	**:**	**1**
R = NO_2 (13, 18, 19)	**1**	**:**	**9**

Scheme 5.



R= NO_2, SO_2F, SO_2CF_3, $SO_2OCH_2CF_3$
Y=Z=H; Y=H, Z=CF_3; Y=CF_3, Z=H

Scheme 6. Binding and atom numeration in calculated anionic σ-complexes.

($\angle$C4C3C2C6 = 10.4, C4C5C6C2 = −6.0°). The CF_3 group in the ring requires more place than the hydrogen atom. Therefore, in the structure calculated for **19** two nitro groups in positions 2 and 4 (Fig. 1) are noticeably rotated out of the ring plane (approx. by 44–48 and 26–28 degrees, respectively). Such a conformation is quite different to that found for the *gem*-bis-CF_3-substituted derivative **18** (Fig. 1) for which an almost planar ring has been found with all NO_2 groups almost co-planar with the ring π-system. It belongs to the C_2 symmetry point group, with the rotational axis going trough C1 and C4 atoms. Two equivalent C-CF_3 bonds are slightly elongated (1.598 Å).

In contrast to the NO_2 substituent, the SO_2F group is not planar, and hence, sterically more demanding. In **6** (C_s symmetrical structure, Fig. 2) the mutual repulsion between the CF_3 group and fluorine atoms of the *ortho*-SO_2F substituents increases the boat-type distortion at the rostrum of the boat ($\angle$C1C2C3C5 = 20.6°, $\angle$C4C3C2C6 = −8.6°). Noteworthy, another (unsymmetrical) conformational form of **6** with one SO_2F group rotated by 180 degrees (**6a**, not shown here, see Supplementary Materials for detailed data) possesses almost the same total energy.

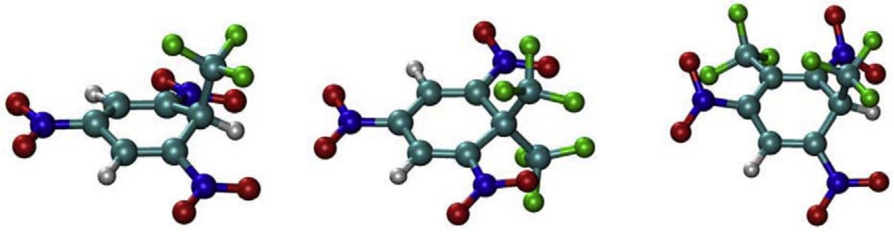
The SO_2CF_3 groups in **4** are sterically more demanding than the SO_2F groups in **6**. In the most favored equilibrium structure of **4** (Fig. 3) the SO_2CF_3 substituents are *trans*-oriented relative to the trifluoromethyl moiety attached to the ring. The C_s symmetrical equilibrium structure of **4** is also boat-like ($\angle$C1C2C3C5 = 20.1°, $\angle$C4C3C2C6 = −8.4°) and therefore similar to that of **6**.

Increasing the substituent to OCH_2CF_3 does not significantly change the most favorable gas-phase conformation for **8** (Fig. 4). The optimized structure still keeps C_s symmetry. As already mentioned by discussing the experimental results, the anions based on the tris-$CF_3CH_2OSO_2$-substituted benzene are especially stable. As it is seen from Fig. 4, in the anionic σ-complex **8** the CF_3 group attached to the ring is shielded with the CF_3CH_2O substituents. The latter are acid enough to build H-bonds towards fluorine atoms, resulting in additional stabilization of **8**.

An introduction of an additional CF_3 group into the fluorinated trifluromethyl derivatives **4**, **6** and **8** provides more diversity for the structures of the corresponding anions. Three main factors affect the structures of anions investigated. These are (a) forming a maximal number of the H-bonds; (b) mutual repulsion between the electron acceptor groups and (c) keeping the in-plane conformation for the electron acceptor groups, providing a maximal delocalization of the negative charge. The combination of these, sometimes oppositely influencing factors provides interesting structural effects.

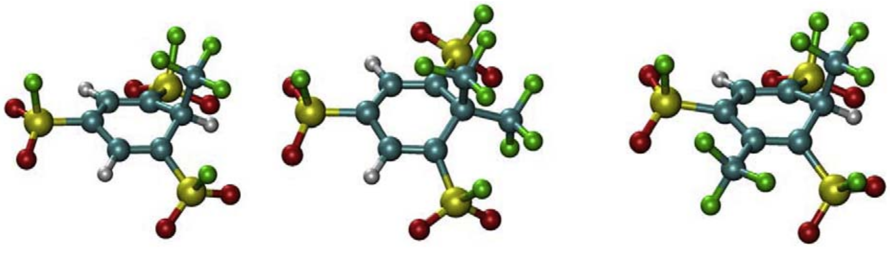
The *gem*-disubstituted anion **14** (Fig. 2) keeps C_s symmetry as well as the overall structure of the starting compound **6**. It possesses the boat-like distorted geometry ($\angle$C1C2C3C5 = 20.0°, $\angle$C4C3C2C6 = −7.4°). The isomeric σ-complex **15** is even more boat-like distorted ($\angle$C1C2C3C5 = 26.8°, $\angle$C1C6C5C3 = −26.1°, $\angle$C4C3C2C6 = −5.2°, $\angle$C4C5C6C2 = 10.8°). While the CF_3 group attached to carbon C3 is not so strongly pressed out from the ring level as it was found for **19** ($\angle C^{(CF_3)}$C3C4C5 = 167.0°), another type of distortion, deviations of SC4C3 and SC4C5 bond angle values from 120 degrees (126.8 and 113.3 degrees, respectively) has been predicted by calculations.

Structures **20** and **21**, while not synthesized, have been investigated theoretically, too. Two most favorable conformations have been found for the bis-substituted *gem*-derivative, **20** (Fig. 3) and **20a** (see Supplementary Material), which lie very close in energy (Δ*E*(RI-MP2) = 0.1 kcal/mol). The structures differ only in conformations of the SO_2CF_3 group in positions 4. Both structures indicate the almost ideally planar rings and slightly different C1–CF_3 bond lengths (approx. 1.55 and 1.58 Å for the CF_3 group *cis*- and *trans*-oriented relative to the o-$(SO_2)CF_3$ moieties. The isomeric



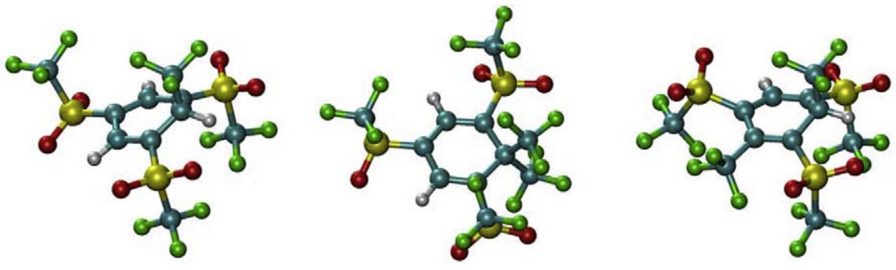
10 **18** **19**

Fig. 1. VMD view for equilibrium (RI-MP2/TZVP) structures of **10**, **18** and **19**.



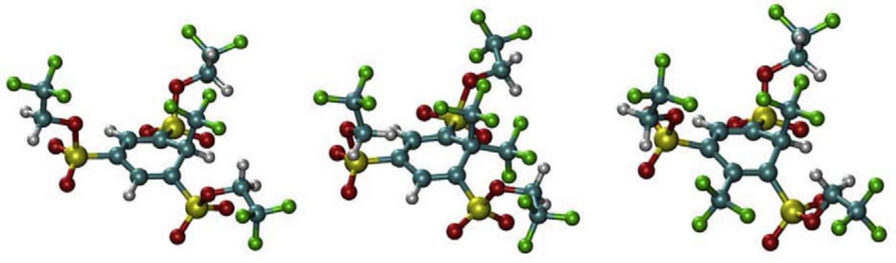
6 **14** **15**

Fig. 2. VMD view for equilibrium (RI-MP2/TZVP) structures of **6**, **14** and **15**.



4 **20** **21**

Fig. 3. VMD view for equilibrium (RI-MP2/TZVP) structures of **4**, **20** and **21**.



8 **16** **17**

Fig. 4. VMD view for equilibrium (RI-MP2/TZVP) structures **8**, **16** and **17**.

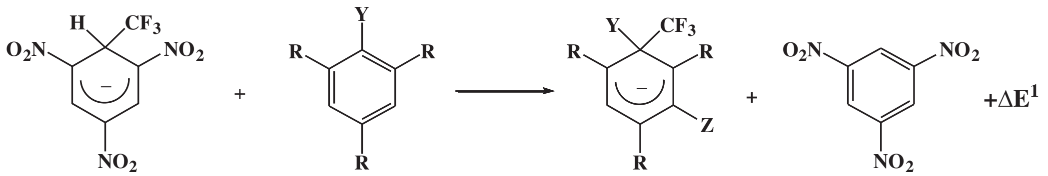
anion **21** is again boat-like distorted (∠C1C2C3C5 = 24.2°, ∠C1C6C5C3 = −24.5°, ∠C4C3C2C6 = −9.7°, ∠C4C5C6C2 = 9.9°, ∠SC4C3 = 129.6°, ∠SC4C5 = 114.5°), probably due to the larger volume of the SO_2CF_3 group compared to the SO_2F moiety.

The corresponding *gem*-bis-CF_3-substituted derivative **16** can probably exist in several different conformations possessing similar (within 1 kcal/mol) total energies. Taking into account the restricted accuracy inherent to the used DFT calculation level or even to the MP2 approach we cannot make a final choice between the various isomers arising due to rotation of substituents. As the examples, two different structures of **16** have been localized as main minima in energy. One of them is shown in Fig. 4 and possesses the C_s symmetrical boat conformation (∠C1C2C3 C5 = 20.9°, ∠C4C3C2C6 = −7.8°). Another one, **16a** (see Supplementary Material) differs from **16** only by *trans*-orientation of the *ortho*-O-CH_2CF_3 groups. Most likely, the conformation of **16** results from a combination of several effects such as a favorable H-bonding, and a sterical repulsion between electronegative atoms.

Similarly, for the isomeric unsymmetrical σ-complex **17** some different conformations can be also localized as the favorable gas-phase structures, depending on the position of the *ortho*-CF_3CH_2O groups. One of them is shown in Fig. 4, the slightly less favored ones are shown in Supplementary Material. Again, the conformation of **17** indicates significant difference of the sp^2 bond angles (SC4C3 = 127.5 and SC4C5 = 112.8 degrees). Noteworthy is the significant different lengths of the C2–C3 (1.396 Å) and C5–C6 bonds (1.364 Å) that can also be resulted from the mutual repulsion between the electron withdrawing CF_3CH_2O and CF_3 moieties.

3.1. Relative stabilities of the anionic σ-complexes

We have compared stabilities of all calculated adducts involving SO_2X substituents with those inherent to the corresponding trinitro-derivatives (Table 3), estimated from the isodesmic reaction (1). As expected, the former are in all cases more stable than the latter (negative vales of ΔE^1, Table 3), due to the more pronounced electron withdrawing properties of the SO_2X substituents compared to those of NO_2. The most stable mono-CF_3 adduct is **4** (ΔE^1 = −11.0 kcal/mol), however introducing a second trifluoromethyl group is more favorable in the case of the SO_2F-substituted species **14** and **15** than for **20** and **21** involving SO_2CF_3 groups (ΔE^1 −9.4 vs. −4.8 kcal/mol for the corresponding *gem*-disubstituted adducts **14** and **20** and −15.3 vs. −13.6 kcal/mol for the unsymmetrical adducts **15** and **21**). Probably, the SO_2CF_3 indicates a stronger sterical repulsion from the CF_3 groups attached to the ring than that inherent to the SO_2F–CF_3 pair.



(1)

For all considered cases the unsymmetrically substituted anions are thermodynamically more stable than the isomeric *gem*-bis-CF_3 anionic species (see Table 3, ΔE^2 magnitudes). This is qualitatively in line with the experimental data. The reaction of 2,4,6-trinitrobenzotrifluoride **13** with Me_3SiCF_3/Me_4NF results in thermodynamically more stable **19** as a main product and the isomeric *gem*-disubstituted anion **18** arises only as traces. Similarly, 2,4,6-tris(fluorosulfonyl)benzotrifluoride **11** yields in the same reaction **15** in the large excess. Only for sulfonyl ester **12** the formation of the *gem*-disubstituted product **16** (90 mol.%) was

Table 3
Relative energy values calculated at the RI-MP2/TZVP//RI-BP86/TZVP level of theory.

Structure	R	ΔE^1, kcal/mol	ΔE^2, kcal/mol
10	NO_2	0.00	–
18		7.9	0.0
19		1.0	−6.8
6	SO_2F	−10.0	–
14		−9.4	0.0
15		−15.3	−6.0
4	SO_2CF_3	−11.0	–
20		−4.8	0.0
21		−13.6	−9.0
8	$SO_2OCH_2CF_3$	−1.8	–
16		−1.8	0.0
17		−5.4	−3.6

proved, while the RI-MP2 calculations still predict a slightly higher stability for the isomeric unsymmetrically substituted anion **17**. At the first look, the experimental data are in contradiction with the relative energy values calculated theoretically. We can exclude that our gas phase RI-MP2/TZVP calculations yield enough exact total energy values, on the other hand, it is noteworthy that the predicted differences in total energies favoured the unsymmetrically disubstituted product, in accord with the experimentally observed trend, decreasing in the order $X = SO_2CF_3 > NO_2 > SO_2F > SO_2OCH_2CF_3$. The preferred formation of **16** vs. **17** could mean the mixed (thermodynamic and kinetic) control of the trifluoromethylation reaction, the detailed investigation of this aspect is however beyond the scope of the current paper and can be a subject of future investigations.

4. Conclusions

A convenient synthetic procedures have been described to obtain gem-trifluoromethyl anionic σ-complexes of 1,3,5-tris(fluorosulfonyl)benzene, 1,3,5-tris(β,β,β-trifluoroethoxysulfonyl)benzene, 1,3,5-tris(trifluoromethylsulfonyl)benzene as well as of 1,3,5-trinitrobenzene. Conditions for easy oxidation of these adducts into corresponding 2,4,6-tris(substituted)benzotrifluorides have been found. The latter add trifluoromethyl anion to the 1 and 3 positions of the aromatic ring forming new anionic σ-complexes (gem-disubstituted and unsymmetrical ones, respectively) in different ratio. Quantum chemical calculations predict different equilibrium structures for the anionic σ-complexes, depending on the nature of the acceptor groups in the ring. The unsymmetrical bis-trifluoromethylated anionic adducts seem in all cases to be significantly more stable than the corresponding gem-disubstituted isomers, while the both structures have been identified in the experiment. This makes it possible to suggest the reaction of trifluoromethylation to be kinetically controlled.

5. Experimental section

General: All reactions were carried out under a dry argon atmosphere by using Schlenk techniques. Me_3SiCF_3 was purchased from ABCR. Me_4NF was synthesized according to literature procedure [15]. All solvents were purified according to procedures described in reference [16]. ^1H, ^{19}F, ^{13}C NMR spectra were recorded on the Varian VXR 300 (299.9 MHz), Varian Gemini 200 (188.1 MHz), and Bruker Avance DRX 400 (100.623 MHz) spectrometers, respectively. Chemical shift values are given in ppm relative to Me_4Si and CCl_3F as external standards. Melting points were measured on the electro-thermal apparatus and are uncorrected.

5.1. Interaction of 1,3,5-tris(trifluoromethylsulfonyl)benzene 1 with $[Cs([15]crown\text{-}5)_2][Me_3Si(CF_3)_2]$

To a well-stirred mixture of CsF (0.24 g, 1.58 mmol) and 15-crown-5 (0.7 g, 3.16 mmol) in DME (15 mL) at −60 °C Me_3SiCF_3 (0.50 g, 3.48 mmol) was added slowly dropwise. The mixture was stirred for 2 h at −30 ÷ −40 °C and then 1,3,5-tris(trifluoromethylsulfonyl)benzene **1** (0.60 g, 1.26 mmol) was added. The mixture formed was stirred for 2 h at −50 ÷ −40 °C and then for 2 h at −30 ÷ −15 °C. After that the reaction mixture was allowed to warm to the room temperature with stirring in bath overnight. The solvent and other volatile materials were evaporated in vacuo at room temperature. The oily residue was washed with Et_2O (3 × 5 mL) and the mixture of *cesium 1-trifluoromethyl-2,4,6-tris(trifluoromethylsulfonyl)cyclohexadienate (***4***)* and *cesium 1,2-bis(trifluoromethyl)-4,6-bis(trifluoromethylsulfonyl)cyclohexadienate (***5***)* (total yield 75%, in ratio 4:1) was precipitated from Et_2O solution as a dark-orange solid. ^1H, ^{19}F and ^{13}C NMR data, see Tables 1 and 2.

5.2. Interaction of 1,3,5-tris(fluorosulfonyl)benzene 2 with $[Me_4N][Me_3Si(CF_3)_2]$

To a well-stirred mixture of Me_4NF (0.05 g, 0.53 mmol) in DME (5 mL) at −60 °C Me_3SiCF_3 (0.17 g, 1.17 mmol) was added slowly dropwise. The mixture was stirred for 1 h at −60 ± 5 °C and then 1,3,5-tris(fluorosulfonyl)benzene **2** (0.15 g, 0.46 mmol) was added. The mixture formed was stirred for 1 h at −50 ± 5 °C and then was allowed to warm to the room temperature with stirring in bath overnight. The solvent and other volatile materials were evaporated in vacuo at room temperature. The oily residue was washed with Et_2O (3 × 5 mL) and *tetramethylammonium 1-trifluoromethyl-2,4,6-tris(fluorosulfonyl)cyclohexadienate (***6***)* with inseparable and unidentified impurity was precipitated from Et_2O solution as a yellow solid. The content of the major product **6** is 85–90%. The yield of **6** is 65% relative to C_6H_5F as internal standard. ^1H, ^{19}F and ^{13}C NMR data, see Tables 1 and 2.

5.3. Tetramethylammonium or potassium 3,5-bis(fluorosulfonyl)benzenesulfonate (7)

To a well-stirred solution of appropriate reagent (Me_4NF (0.31 mmol) in DME (2 mL) or $KHCO_3$ (0.31 mmol) in DMSO-d_6 (2 mL)) 1,3,5-tris(fluorosulfonyl)benzene **2** (0.10 g, 0.31 mmol) was added. The mixture was stirred at room temperature overnight. The product formation was monitored by ^1H, ^{19}F and ^{13}C NMR spectrometry. (In the case of the reaction in DME solvent was evaporated in vacuo and the residue was dissolved in DMSO-d_6). ^1H NMR (299.9 MHz, DMSO-d_6): δ 8.73 (1H, s, H-4), 8.57 (2H, s, H-2 and H-6). ^{19}F NMR (188.1 MHz, CCl_3F): δ 66.05 (s, 2F, SO_2F). ^{13}C NMR (100.623 MHz, DMSO-d_6): δ 53.11 (s, C-1), 134.61 (d, $^2J_{C,F}$ = 28.1 Hz, C-3,5), 132.26 (s, C-2,6), 128.92 (s, C-4).

5.4. General procedure for the synthesis of the anionic σ-complexes (8) and (10)

To a well-stirred solution of appropriate substrate **3** or **9** (0.35 mmol) in DME (4 mL) at −60 °C Me_3SiCF_3 (0.06 g, 0.45 mmol) and Me_4NF (0.04 g, 0.42 mmol) were added. The mixture was stirred for 1 h at −50 ± 5 °C and allowed to warm to room temperature with stirring in bath overnight. The solvent and other volatile materials were evaporated in vacuo at room temperature. The oily residue was washed with Et_2O (3 × 5 mL) and the product was precipitated from Et_2O solution.

5.4.1. Tetramethylammonium 1-trifluoromethyl-2,4,6-tris(β,β,β-trifluoroethoxysulfonyl)cyclohexa-dienate (8)

Yield: 0.23 g (95%), a yellow solid, mp 71–72 °C. Anal. Calcd. for $C_{17}H_{21}F_{12}NO_9S_3$: C, 28.84; H, 2.99; F, 32.24; N, 1.9; S, 13.6. Found:

C, 28.61; H, 3.12; N, 2.1; F, 32.51; S, 13. 48. ^{1}H, ^{19}F and ^{13}C NMR, see Tables 1 and 2.

5.4.2. Tetramethylammonium 1-trifluoromethyl-2,4,6-trinitrocyclohexadienate (10)

Yield: 0.11 g (95%), dark-red solid, mp 170–171 °C. Anal. Calcd. for $C_{11}H_{15}F_3N_4O_6$: C, 37.06; H, 4.24; F, 16; N, 15.73. Found: C, 36.9; H, 4.17; F, 15.92; N, 15.54. ^{1}H, ^{19}F and ^{13}C NMR data, see Tables 1 and 2.

5.5. General procedure for the oxidation of the anionic σ-complexes (6), (8) and (10)

To a well-stirred solution of appropriate substrate **6**, **8** or **10** (1.1 mmol) in DME (10 mL) at 0 ± 5 °C *t*-BuOCl (0.15 g, 1.43 mmol) was added. The mixture was stirred for 5–10 min at present temperature and allowed to warm to room temperature with stirring. The residue formed was filtered off and the solid was washed with DME (2 × 5 mL). The solvent was evaporated in vacuo. The crude product was crystallized from appropriate solvent.

5.5.1. 2,4,6-Tris(fluorosulfonyl)benzotrifluoride (11)

The crude product was crystallized from CCl_4. Yield: 0.32 g (75%), white solid, mp 103–105 °C. ^{1}H NMR (299.9 MHz, THF-d_8): δ 9.2 (2H, s, H-3 and H-5). ^{19}F NMR (188.1 MHz, CCl_3F): δ −53.45 (t, $^{5}J_{F,F} = 16$ Hz, 3F, CF_3), 64.86 (s, 1F, *p*-SO_2F), 64.31 (q, $^{5}J_{F,F} = 16$ Hz, *o*-SO_2F). ^{13}C NMR (100.623 MHz, THF-d_8): δ 139.28 (s, C-3 and C-5), 139.13 (d, $^{2}J_{C,F} = 31.7$ Hz, C-4), 138.72 (d, $^{2}J_{C,F} = 31.7$ Hz, C-2 and C-6), 136.548 (q, $^{2}J_{C,F} = 38.24$ Hz, C-1). 121.38 (q, $^{1}J_{C,F} = 277$ Hz, CF_3). Anal. Calcd. for $C_7H_2F_6O_6S_3$: C, 21.42; H, 0.5; F, 29.06; S, 24.53. Found: C, 21.21; H, 0.42; F, 29.23; S, 24.67.

5.5.2. 2,4,6-Tris(β,β,β-trifluoroethoxysulfonyl)benzotrifluoride (12)

The crude product was crystallized from benzene. Yield: 0.63 g (90%), white solid, mp 164–165 °C. ^{1}H NMR (299.9 MHz, THF-d_8): δ 9.01 (2H, s, H-3 and H-5), 5.27 (4H, q, $^{3}J_{H,F} = 8.4$ Hz, *o*-$SO_3CH_2CF_3$), 5.12 (2H, q, $^{3}J_{H,F} = 8.4$ Hz, *p*-$SO_3CH_2CF_3$). ^{19}F NMR (188.1 MHz, CCl_3F): δ −53.99 (s, 3F, CF_3), −75.08 (m, 9F, $SO_3CH_2CF_3$). ^{13}C NMR (100.623 MHz, THF-d_8): δ 141.51 (s, C-4), 141.4 (q, $^{3}J_{C,F} = 1.9$ Hz C-2 and C-6), 137.09 (s, C-3 and C-5), 134.48 (q, $^{2}J_{C,F} = 37.73$ Hz, C-1), 123.53 (q, $^{1}J_{C,F} = 277.22$ Hz, *p*-$SO_3CH_2CF_3$), 123.52 (q, $^{1}J_{C,F} = 277.5$ Hz, *o*-$SO_3CH_2CF_3$), 121.82 (q, $^{1}J_{C,F} = 277.5$ Hz, CF_3), 67.68 (q, $^{2}J_{C,F} = 38$ Hz, *o*-$SO_3CH_2CF_3$), 67.41 (q, $^{2}J_{C,F} = 38$ Hz, *p*-$SO_3CH_2CF_3$). Anal. Calcd. for $C_{13}H_8F_{12}O_9S_3$: C, 24.7; H, 1.27; F, 36.1; S, 15.2. Found: C, 24.91; H, 1.33; F, 35.93; S, 15. 43.

5.5.3. 2,4,6-Trinitrobenzotrifluoride (13)

The crude product was crystallized from benzene. Yield: 0.27 g (85%); a white solid; mp 87–88 °C. ^{1}H NMR (299.9 MHz, DMSO-d_6): δ 8.78 (2H, s, H-3 and H-5). ^{19}F NMR (188.1 MHz, CCl_3F): δ −59.62 (s, 3F, CF_3). ^{13}C NMR (100.623 MHz, DMSO-d_6): δ 150.63 (s, C-2 and C-6), 150.1 (s, C-4), 122.86 (s, C-3 and C-5), 126.6 (q, $^{1}J_{C,F} = 288.28$ Hz, CF_3), 122.68 (q, $^{2}J_{C,F} = 36.02$ Hz, C-1). Anal. Calcd. for $C_7H_2F_3N_3O_6$: C, 29.89; H, 0.72; F, 20.28; N, 14.95. Found: C, 30.05; H, 0.84; F, 20.52; N, 15.03.

5.6. Interaction of 2,4,6-tris(fluorosulfonyl)benzotrifluoride 11 with [Me_4N][$Me_3Si(CF_3)_2$]

To a well-stirred mixture of Me_4NF (0.08 g, 0.88 mmol) in DME (9 mL) at −60 °C Me_3SiCF_3 (0.27 g, 1.93 mmol) was added slowly dropwise. The mixture was stirred for 1 h at -60 ± 5 °C and then 1,3,5-tris(fluorosulfonyl)benzotrifluoride **11** (0.3 g, 0.76 mmol) was added. The mixture formed was stirred for 1 h at -55 ± 5 °C and then was allowed to warm to room temperature with stirring in bath overnight. The solvent and other volatile materials were evaporated in vacuo at room temperature. The oily residue was washed with Et_2O (3 × 5 mL) and the mixture of *tetramethylammonium 1,1-bis(trifluoromethyl)-2,4,6-tris(fluorosulfonyl)cyclohexadienate* (**14**) and *tetramethylammonium 1,3-bis(trifluoromethyl)-2,4,6-tris(fluorosulfonyl)-cyclohexadienate* (**15**) in ratio 1:2 correspondingly in total yield 85% relative to C_6H_5F as an internal standard were precipitated from Et_2O solution as a yellow solid. ^{1}H, ^{19}F and ^{13}C NMR data, see Tables 1 and 2.

5.7. General procedure for the interaction of benzotrifluorides 12 and 13 with Me_3SiCF_3/F^- system

To a well-stirred solution of appropriate substrate **12** or **13** (0.47 mmol) in DME (10 mL) at −60 °C Me_3SiCF_3 (0.08 g, 0.59 mmol) and Me_4NF (0.05 g, 0.54 mmol) were added. The mixture was stirred for 1 h at -50 ± 5 °C and allowed to warm to room temperature with stirring in bath overnight. The solvent and other volatile materials were evaporated in vacuo at room temperature. In the case of **12** the oily residue was washed with Et_2O (3 × 5 mL) and the product was precipitated from Et_2O solution.

5.7.1. Tetramethylammonium 1,1-bis(trifluoromethyl)-2,4,6-tris(β,β,β-trifluoroethoxysulfonyl)cyclohexadienate (16) and tetramethylammonium 1,3-bis(trifluoromethyl)-2,4,6-tris(β,β,β-trifluoroethoxysulfonyl)cyclohexadienate (17)

The products **16** and **17** were obtained in ratio 9:1 correspondingly in total yield 95% relative to C_6H_5F as an internal standard. Product **16** was precipitated from Et_2O solution. Yield: 0.25 g (67%), yellow solid, mp 109–110 °C. Anal. Calcd. for $C_{18}H_{20}F_{15}O_9S_3$: C, 29.69; H, 2.77; F, 39.18; S, 13.22. Found: C, 23.21; H, 2.81; F, 39.63; S, 13. 33. ^{1}H, ^{19}F and ^{13}C NMR data, see Tables 1 and 2.

5.7.2. Tetramethylammonium 1,1-bis(trifluoromethyl)-2,4,6-trinitrocyclohexadienate (18) and tetramethylammonium 1,3-bis(trifluoromethyl)-2,4,6-trinitrocyclohexadienate (19)

The products **18** and **19** were obtained in ratio 1:9 correspondingly in total yield 70% relative to C_6H_5F as an internal standard. ^{1}H and ^{19}F NMR data, see Table 1.

6. Theoretical section

All the structures were first optimized using TURBOMOLE (version 6.02) program packet [17], and the implemented Resolution Identity (RI) [18] algorithm. RI-BP86 functional [19,20] and standard triple-zeta basis sets [21] (TZVP) were used. The contraction of the basis functions were (14s9p)/[5s4p] → {73211/6111} for S, (11s6p)/[5s3p] → {62111/411} for C, N,O and F and (5 s)/[3 s] → {311} for H. One set of (five) d-functions was added for every non-hydrogen atom and one set of p-functions was used for H's. For all the structures vibrational analyses were performed computing numerically first and second order derivatives, checking the equilibrium structures to be true local minima in energy. The most favorable structures were re-optimized using the more superior RI-MP2 method [22,23] within the frozen core approximation. The same (TZVP) basis sets were used. No frequency analyses were performed at this level of approximation. The relative energy values were calculated from the total RI-MP2/TZVP energy magnitudes without zero-point energy corrections. The optimized structures were pictured using the VMD program [24].

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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.2010.09.005.

References

[1] (a) M.J. Strauss, Chem. Rev. 70 (1970) 667–712;
(b) F. Terrier, Chem. Rev. 82 (1982) 77–152;
(c) G.A. Artamkina, G. Egorov, I.P. Beletskaja, Chem. Rev. 82 (1982) 427–459;
(d) V.N. Knyazev, V.N. Drozd, Zh. Org. Khim. 31 (1995) 3;
(e) E. Buncel, J.M. Dust, F. Terrier, Chem. Rev. 95 (1995) 2261–2280.

[2] (a) S.S. Gitis, A.Ya. Kaminskii, Usp. Khim. 47 (1978) 1970–2013;
(b) P.P. Onys'ko, N.V. Proklina, Yu.G. Gololobov, Zh. Org. Khim. 21 (1985) 1647–1652;
(c) M.P. Simonnin, J.C. Halle, F. Terrier, M.J. Pouel, Can. J. Chem. 63 (1985) 866–870;
(d) A.K. Sheinkman, T. Nezdiminoha, T.S. Chmilenko, Zh. Org. Khim. 21 (1985) 668–669;
(e) P.J. Atkins, V. Gold, P.J. Routledge, J. Chem. Soc. Perkin Trans. 2 10 (1985) 1563–1566;
(f) G.A. Artamkina, S.V. Kovalenko, I.P. Beletskaja, O.A. Reutov, J. Organometal. Chem. 392 (1987) 139–150;
(g) E. Buncel, J.M. Dust, R.A. Manderville, K.T. Park, I. Onyldo, Bull. Soc. Chim. France 2 (1988) 371–376;
(h) G.P. Stahly, J. Fluorine Chem. 45 (1989) 431–433;
(i) S.V. Kovalenko, G.A. Artamkina, P.B. Terent'ev, V.K. Shevtsov, I.P. Beletskaja, O.A. Reutov, Khimija Geterots. Soedin. 3 (1990) 412–416;
(j) L. Gallardo, G. Guirado, J. Marquet, J. Org. Chem. 67 (2002) 2548;
(k) L. Gallardo, G. Guirado, J. Marquet, J. Org. Chem. 68 (2003) 7334–7341;
(l) M. Suroviec, M. Makosza, Tetrahedron 60 (2004) 5019–5024.

[3] (a) L.M. Yagupolskii, V.N. Boiko, G.M. Shchupak, N.V. Kondratenko, V.P. Samur, Tetrahedron Lett. (1975) 4413–4414;
(b) V.N. Boiko, N.V. Ignat'ev, G.M. Shchupak, L.M. Yagupolskii, Zh. Org. Khim. 15 (1979) 806–816;
(c) N.V. Ignat'ev, V.N. Boiko, L.M. Yagupolskii, Zh. Org. Khim. 16 (1980) 1501–1508;
(d) I.M. Sosonkin, V.N. Boiko, N.V. Ignat'ev, L.M. Yagupolskii, Zh. Org. Khim. 18 (1982) 2385–2388.

[4] (a) J.T. Welch, S. Eswaarakrishnan, Fluorine in Bioorganic Chemistry, Wiley, New York, 1991;
(b) T. Hiyama, Organofluorine Compounds: Chemistry and Applications, Springer, Berlin, 2000;
(c) P. Kirsch, Modern Fluoroorganic Chemistry, Wiley-WCH, Weinheim, 2004;
(d) J.-P. Begue, D. Bonnet-Delpon, Bioorganic and Medicinal Chemistry of Fluorine, Wiley, New Jersey, 2008.

[5] (a) R.P. Singh, J.M. Shreeve, Tetrahedron 56 (2000) 7613–7632;
(b) J.K.S. Prakash, A.K. Yudin, Chem. Rev. 97 (1997) 757–786;
(c) G.G. Furin, Zh. Org. Khim. 33 (1997) 1287–1319.

[6] A.A. Kolomeitsev, V.N. Movchun, Yu.L. Yagupolskii, Tetrahedron Lett. 33 (1992) 6191–6192.

[7] V.N. Boiko, A.A. Filatov, Yu.L. Yagupolskii, V.D. Prisyazhnii, S.I. Chernuhin, D.O. Tret'yakov, U.A. Patent 72649, 2005.

[8] V.N. Boiko, A.A. Filatov, O.M. Kamoshenkova, Yu.L. Yagupolskii, 7 Vserosijyskaja Konferentsiya "Khimija Ftora", Moskow, Russia, Abstract of Papers, 2006, P-07.

[9] (a) L.M. Yagupolskii, A.Y. Il'chenko, N.V. Kondratenko, Chem. Rev. [USSR] 43 (1974) 32–47;
(b) C. Hansch, A. Leo, D. Hoekman, Exploring QSRA Hydrophobic, Electronic and Steric Constants, ACS Professional Reference Book, Washington, DC, 1995.

[10] V.N. Boiko, O.M. Kamoshenkova, A.A. Filatov, Tetrahedron Lett. 49 (2008) 2719–2721.

[11] V.I. Popov, V.T. Skrypkina, S.P. Protsyk, A.A. Skrynnikova, B.M. Krasovitskii, L.M. Yagupolskii, Ukr. Khim. Zh. 57 (1991) 843–849.

[12] O.M. Kamoshenkova, V.N. Boiko, J. Fluorine Chem. 131 (2010) 248–253.

[13] (a) N. Maggiarosa, W. Tyrra, D. Naumann, N.V. Kirij, Yu.L. Yagupolskii, Angew. Chem. 111 (1999) 2392–2393, Angew. Chem. Int. Ed. 38 (1999) 2252;
(b) A. Kolomeitsev, G. Bissky, E. Lork, V. Movchun, E. Rusanov, P. Kirsch, G.-V. Röschenthaler, Chem. Commun. 1017–1018 (1999).

[14] W. Tyrra, M.M. Kremlev, D. Naumann, H. Scherer, H. Schmidt, B. Hoge, I. Pantenburg, Yu.L. Yagupolskii, Chem. Eur. J. 11 (2005) 6514–6518.

[15] A.A. Kolomeitsev, F.U. Seifert, G.-V. Röschentalhaler, J. Fluorine Chem. 71 (1995) 47–49.

[16] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, second ed., Pergamon, Oxford, 1980.

[17] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165–169, see also: http://www.ipc.uni-karlsruhe.de/tch/tch1/turbomole/index.en.html and references cited therein.

[18] (a) B.I. Dunlap, J.W.D. Connolly, J.R. Sabin, J. Chem. Phys. 71 (1979) 339;
(b) O. Vahtras, J. Almlöf, M.V. Feyereisen, Chem. Phys. Lett. 213 (1993) 514–518;
(c) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 240 (1995) 283–289.

[19] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[20] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.

[21] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829–5835.

[22] F. Weigend, M. Häser, Theor. Chem. Acc. 97 (1997) 331–340.

[23] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, Chem. Phys. Lett. 294 (1998) 143–152.

[24] VMD for WIN-32, Version 1.8.2 (Dezember 4, 2003) W. Humpfrey, A. Dalke, K. Schulten, J. Mol. Graphics, 14 (1996) 33.