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Calculated structures of thiopyrylium-S-fluoride and S-trifluoride and attempts of their preparation

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Abstract

Structures and energies of cyclo-C_5H_5SF and cyclo-$C_5H_5SF_3$ have been calculated. In both cases the 2- and 4-CF-isomers are more stable than the SF and SF_3 isomers. The fluxional behavior of the sulfur bonded fluorides has been calculated also. In cyclo-C_5H_5SF an ellipsoidal rotation of the sulfur bonded fluorine atom is observed with a barrier of a few kcal mol^{-1}. In sulfur bonded cyclo-$C_5H_5SF_3$ the (Turnstile) rotation is predicted to occur without noticeable barrier, in agreement with previous work.

Attempts to isolate the sulfur bonded isomers failed entirely: always 2 or 4-carbon-fluorides were obtained for cyclo-C_5H_5SF. The acyclic SF_5^- carrying precursors for the synthesis of cyclo-$C_5H_5SF_3$ failed in crucial steps of the reactions.

Keywords: Ab initio calculations; Density functional calculations; Sulfur heterocycles; Sulfur fluorine compounds; NMR spectroscopy

1. Introduction

Thiopyrylium salts have been known for a long time (reviews of thiopyrylium salts [1]), and recently we offered a reliable synthesis starting from readily available precursors [2]. The question arose, what could be the nature of thiopyrylium fluoride, which is not yet known. The known salts have fairly large anions like BF_4^-, I^-, $CF_3SO_3^-$ [2].

It can be envisioned that a thiopyrylium fluoride is a molecular species rather than a salt, and one aim of this work is to predict its structure and isolate it. Thiopyrylium-S-fluoride is a derivative of sulfur(IV), or more precisely, of the sulfur ylid $H_2C{=}SF_2$. This molecule has not yet been prepared, but some derivatives have, $(CF_3)_2C{=}SF_2$ [3], $CF_3(SF_5)C{=}SF_2$ [3], and $C_6F_5{-}N{=}CF{-}(SF_5)C{=}SF_2$ [4], which all have a pyramidal structure at the sulfur atom. $H_2C{=}SF_2$, however, is predicted to have two quite different structures, pyramidal, like the known derivatives, which would be normal, or a planar T shaped, depending on the type of calculation [3,5]. One of the questions is how this structural ambiguity is reflected in thiopyrylium-S-fluoride. Very recently Wang and Ragué Schleyer [6] calculated this molecule in the S–F bonded ground state, as will be discussed later.

Organic sulfur(VI) compounds are often very stable compounds, so even a thiopyrylium-S-trifluoride could exist. This molecule can be considered a derivative of the known alkylidene sulfur tetrafluorides [7], in particular $H_2C{=}SF_4$. These compounds are fairly stable and have a distinct trigonal-bipyramidal geometry in which the carbon atom occupies an equatorial position and the axial fluorine atoms on the sulfur atom occupy positions in the CH_2 plane. If this molecule is built into a six-membered ring, then for the sake of planarity, one of the two axially positioned atoms must be part of the ring.

Previously, Xie et al. have calculated the geometry and energy of this molecule, cyclo-$C_5H_5SF_3$, and arrived at the conclusion that there should exist two isomers which are almost indistinguishable in energy; one is based on a trigonal-bipyramidal environment at sulfur, with a fully planar six-membered ring, and another with a square pyramidal environment around the sulfur atom [8].

Our work follows this prediction, including attempts to prepare such compounds. We include explanations why so far all attempts failed, due to the existence of additional isomers with much lower energy.

2. Theoretical calculations

We have applied basis sets and computational methods that fulfil the requirements of reasonable computation time

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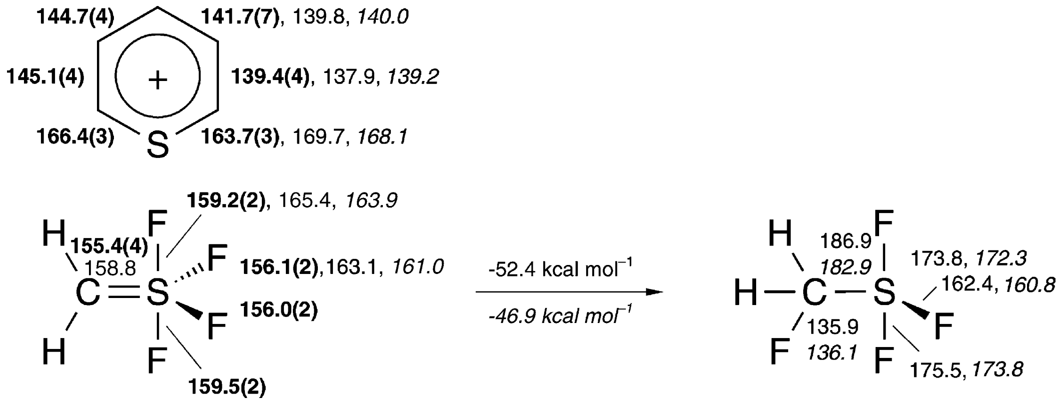


Fig. 1. Results of the calculation in comparison to experimental data. Solid numbers: bond lengths from X-ray single crystal structure determinations [2,12]. Normal numbers: DFT calculation, italics: MP2-ab initio calculations.

and data space for the large number of fairly large molecules in question, and that also reproduce the structure for known molecules, so that reliable results can be anticipated for related, but unknown molecules. We have chosen the often used 6-311 + G(d, p) basis set for all atoms, and the density functional method (DFT) according to Becke [9] including the correlation functional of Lee et al. [10]. The Møller–Plesset second-order perturbation (MP2) on the *Hartree-Fock* calculation was also applied [11], although this method is much more space and time consuming. First we tested the calculations on two model compounds with known structures, cyclo-$C_5H_5S^+$ and $H_2C{=}SF_4$ (see Fig. 1, Table 1). The overall geometries are correctly predicted, while bond lengths towards the sulfur atoms are too long by a few pm, relative bond lengths differences are well predicted. Of importance, as will be obvious later, is also the difference between $H_2C{=}SF_4$ and its 1,2-fluorine shift product, F–CH_2–SF_3 (see Fig. 1). The latter is predicted to be 52.4 kcal mol^{-1} more stable. Nevertheless $H_2C{=}SF_4$ is a quite stable compound at room temperature and has been obtained in large amounts [7].

Table 1
Symmetry and energies of calculated compounds, corrected for zero point energy

Compound	Symmetry	Energy (a.u.)	
		B3LYP	MP2
Cyclo-$C_5H_5S^+$	C_{2v}	−591.442133	−590.297486
$H_2C{=}SF_4$	C_1	−836.829695	−835.342596
F–CH_2–SF_3	C_s	−836.913189	−835.417320
Cyclo-C_5H_5SF	C_s	−691.531112	−690.175562
Cyclo-C_5H_5SF (TS)	C_1	−691.518623	−690.156904
Cyclo-2-F–C_5H_5S	C_s	−691.561373	−690.206301
Cyclo-4-F–C_5H_5S	C_s	−691.558174	−690.202274
Cyclo-$C_5H_5SF_3$ (trigonal-bipyramidal)	C_s	−891.169507	−889.413375
Cyclo-$C_5H_5SF_3$ (square pyramidal)	C_1	−891.169609	−889.413484
Cyclo-2-F–$C_5H_5SF_2$	C_s	−891.243279	−889.478950
Cyclo-4-F–$C_5H_5SF_2$	C_{2v}	−891.241195	−889.479788

2.1. The isomers cyclo-C_5H_5SF

The monofluoride C_5H_5SF can exist in three different isomeric forms, one is S–F bonded, two are C–F bonded (see Fig. 2). 2-Fluoro and 4-fluoro thiopyrane are completely as expected. The S–F bonded isomer has a remarkable structure with a mirror symmetry defined by S, F, and C-4, in full agreement with the recently published results [6]. This structure could be interpreted as a derivative of the pyramidal form of the sulfur ylid $H_2C{=}SF_2$. The inner ring pairwise distances are equal. This isomer can be considered aromatic. For discussion of aromaticity in this and other C_5H_5XY compounds see [6]. If, however, a totally planar molecule is assumed, i.e. a derivative of the planar form of $H_2C{=}SF_2$, then this is a transition state (TS) on the potential hypersurface. It is only 7.8 kcal mol^{-1} higher in energy than the pyramidal structure (see Fig. 2, Table 1).

One can obtain this transition state by a rotation of the fluorine atom around the axis formed the S and the opposite C atom in the ring. Except for the slightly elongated S–F bond in the planar form, all other structural parameters remain essentially unaffected. This movement has been calculated in 5° steps of the rotational angle (see Fig. 3). A smooth curve is obtained. If the energy differences of 7.8 (DFT) or 11.7 kcal (MP2) are real, then the ellipsoidal movement of the fluorine atom should occur at room temperature. The S–F bond distances of 191.1 pm in the ground state and 211.3 pm in the 90° rotamer indicate strong ionic character for the S–F bond. The calculated charge is −0.36 on the F atom for the ground state and −0.58 in the rotamer. The rotamer can be considered close to the transition state of the 1,2-fluorine shift reaction to cyclo-2-F–C_5H_5S, which is about 20 kcal mol^{-1} more stable. This may explain why all attempts have so far failed to isolate cyclo-C_5H_5SF.

2.2. Thiopyrylium-S-trifluoride

Xie et al. have already calculated the geometry and energy of this compound [8], and arrived at the conclusion that there exist two different structures, both with mirror symmetry but

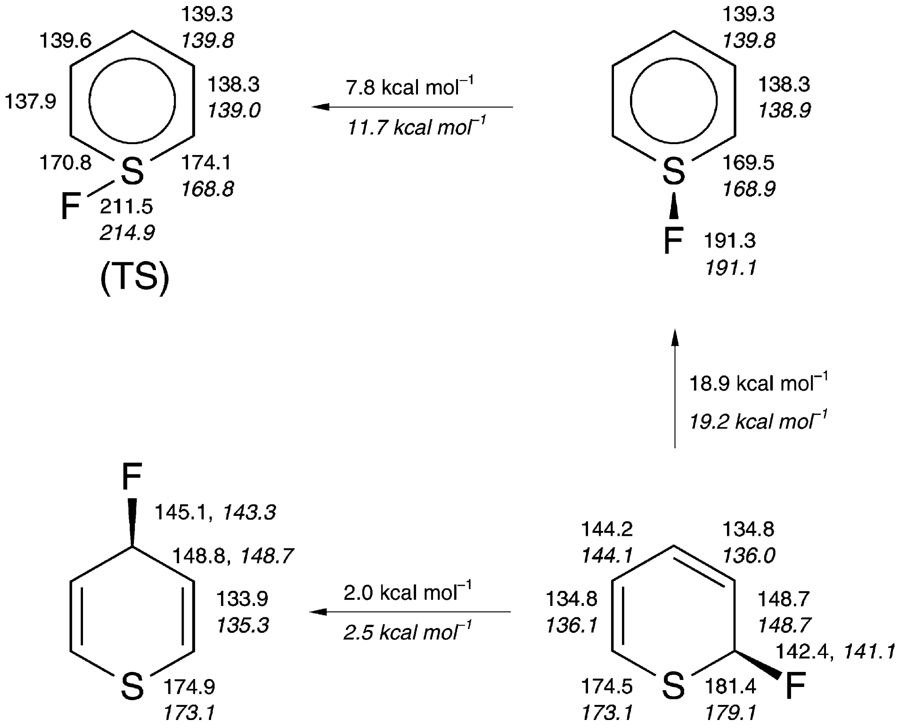


Fig. 2. Calculated structures and relative energies of cyclo-C_5H_5SF isomers. Bond lengths: normal numbers, DFT calculations; italics, MP2-ab initio calculations. TS = fully planar transition state.

with different positions of the fluorine atoms with respect to the C_5S ring plane. The very slightly more stable isomer had a fully planar C_5H_5S ring, one fluorine atom also in the ring plane and a trigonal-bipyramidal overall structure around the sulfur atom. Bond distances within the ring alternate markedly. The other structure is based on a square pyramid around the sulfur atom. Both our DFT and MP2 calculation predict the square pyramidal form to be slightly lower in

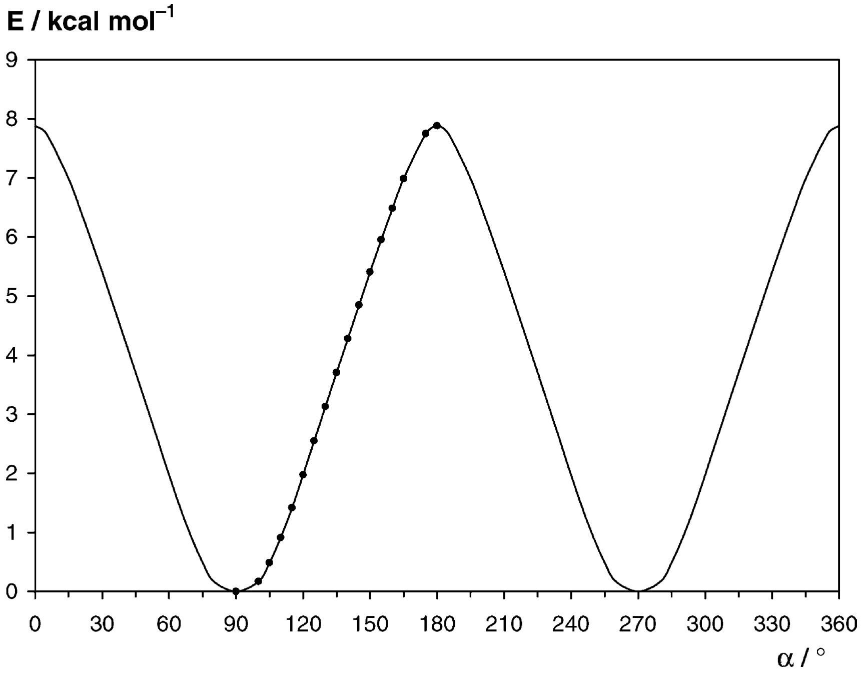


Fig. 3. Calculated energy profile of the ellipsoidal fluorine atom rotation around the sulfur atom in cyclo-C_5H_5SF, DFT calculation. α is defined as the dihedral cycle C_2–C_1–S–F, which is nearly the same as the angle of the S–F bond against the (best) ring lane.

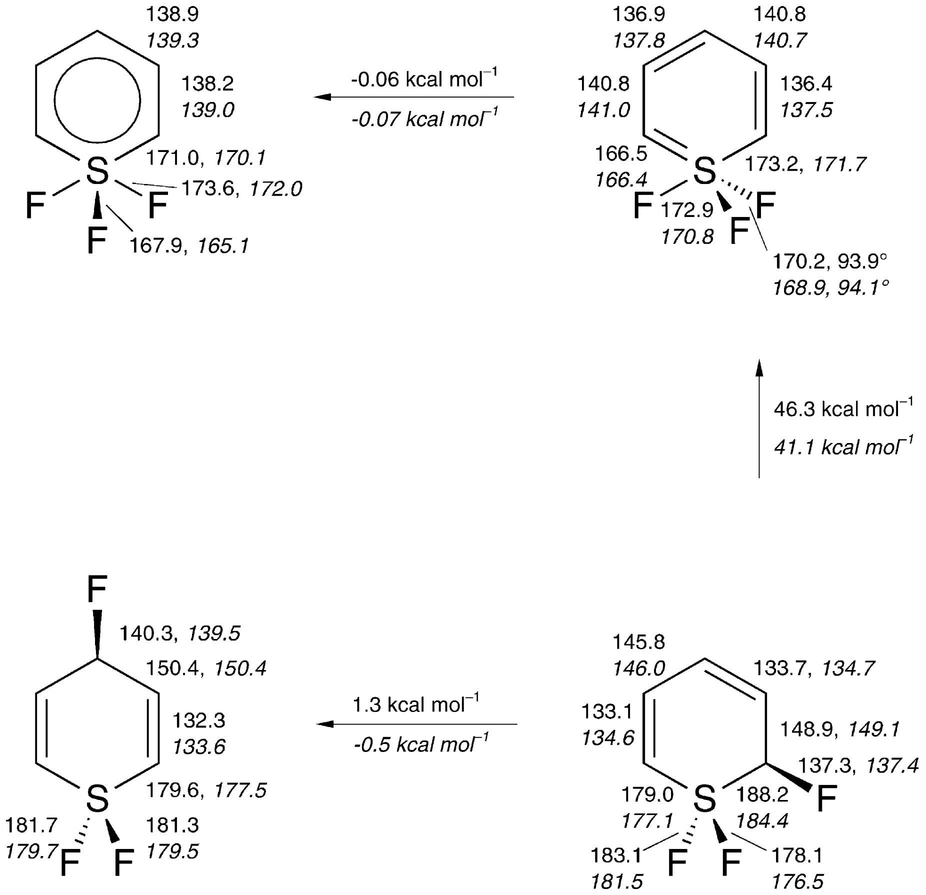


Fig. 4. Calculated structures and relative energies of cyclo-$C_5H_5SF_3$ isomers. Bond lengths: normal numbers, DFT calculations; italics, MP2-ab initio calculations.

energy (see Fig. 4, Table 1). However, the energy difference between the trigonal-bipyramidal and the square pyramidal forms is so small that it must be considered meaningless. So the conclusion first drawn by Xie et al. is still valid, namely that the real minimum energy structure of this molecule is still unclear. We have also calculated the energy as a function of the rotation of the SF_3 group against the ring plane, and there is essentially no barrier towards this rotation. This itself is a remarkable phenomenon, since the movement is exactly what has been described as the turnstile mechanism [13]. Another feature of this molecule is that in the trigonal-bipyramidal structure, the bonds within the ring alternate markedly, while in the square pyramidal structure the C–C bond lengths become very similar, as are the two C–S bond lengths.

Grossly simplified, the bonding situation in the trigonal-bipyramidal ring can be described as that of a (hetero)cyclohexatriene, in the square pyramidal structure as aromatic. The gain of aromatic energy is compensated by a loss of bond energy in the S–F bonds in the square pyramidal structure, and vice versa. The calculated ^{13}C NMR chemical shifts indicate a quite different bonding situation. In particular the ^{13}C NMR values of the carbon atoms adjacent to the sulfur atom are very different (see Fig. 5).

It can be expected that the absorption spectra of these two structural isomers differ markedly, and the possibility cannot be excluded that pulsed energy absorption into the ring of one isomer may induce the turnstile rotation of the SF_3 group as in a molecular propeller.

Nevertheless, these two structures are far away from the true energetic minima, which are 2-F-cyclo-$C_5H_5SF_2$ and 4-F-cyclo-$C_5H_5SF_2$. Both have almost the same energy. Especially the 2-F-cyclo-$C_5H_5SF_2$ can be formed easily by a 1,2-fluorine shift reaction from the trigonal-bipyramidal cyclo-$C_5H_5SF_3$, so that preparation of the latter remains a formidable task.

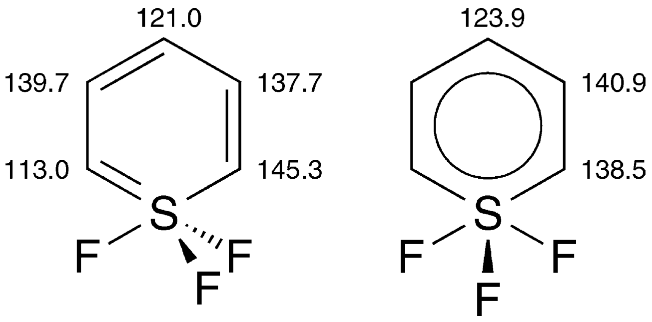
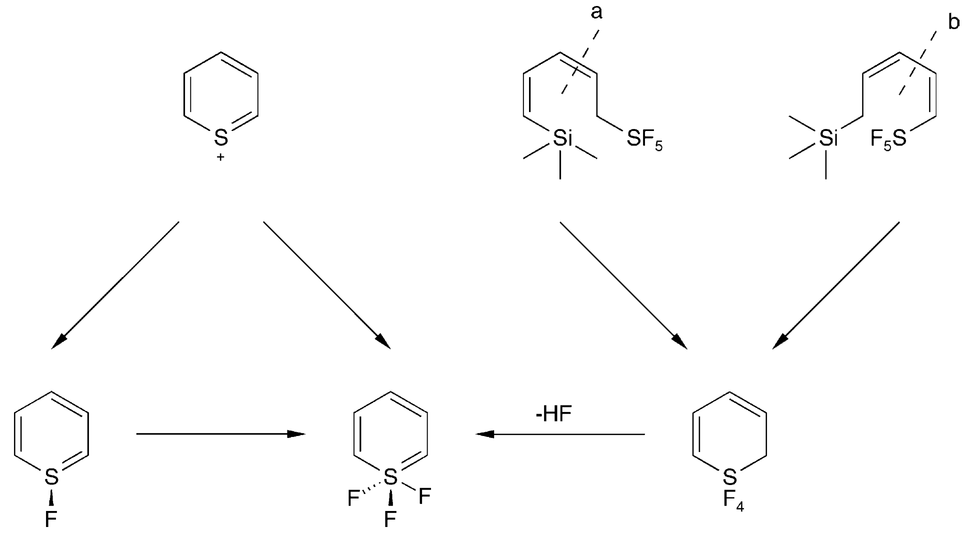


Fig. 5. Calculated NMR chemical shift data for the trigonal-bipyramidal ((hetero)cyclo-hexatriene) and square pyramidal (aromatic) rotamer of cyclo-$C_5H_5SF_3$.



Scheme 1. Concept of syntheses for thiopyrylium-S-fluoride and trifluoride.

3. Attempts to synthesize thiopyrylium-S-fluoride and S-trifluoride

Our synthetic concept for the thiopyrylium-S-fluorides starts with the preformed C_5H_5S six-membered ring. The synthesis of thiopyrylium-S-trifluoride has been attempted by cyclization reactions of difunctional precursors carrying a SF_5 group (Scheme 1).

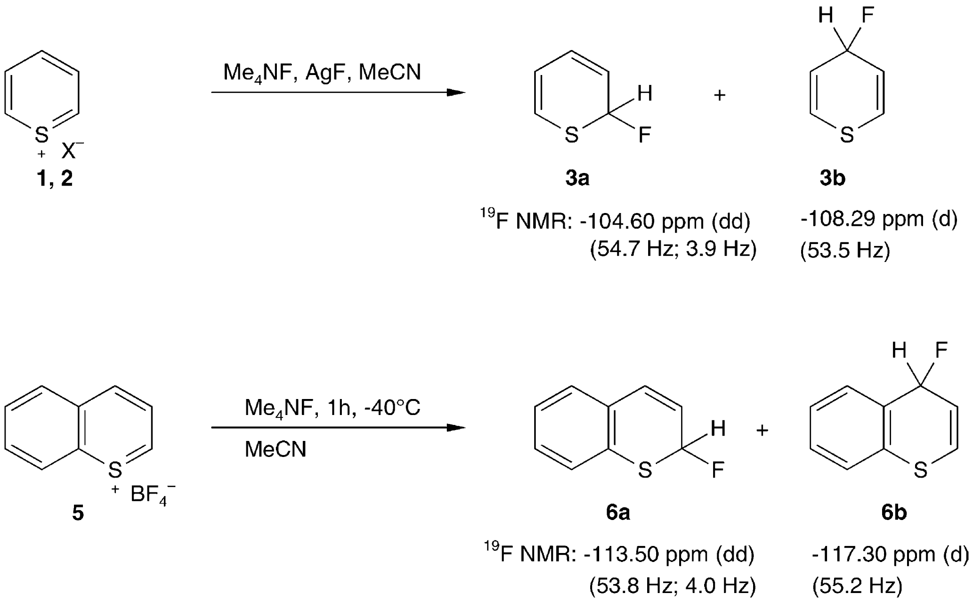
3.1. Attempts with thiopyrylium salts

It was known that strong carbon nucleophiles like aryl or alkyl lithium compounds react with thiopyrylium salts under attack on the sulfur atom, forming aryl or alkyl thiabenzenes. Without electron withdrawing groups in 2 and/or 4 positions in the heterocycle, the thiabenzenes rearrange into 2H- and 4H-thiopyranes. N, S, and O nucleophiles and also weaker C nucleophiles attack thiopyrylium salts in the 2 and 4 position, without a primary attack at the ring sulfur atom [1,14–16].

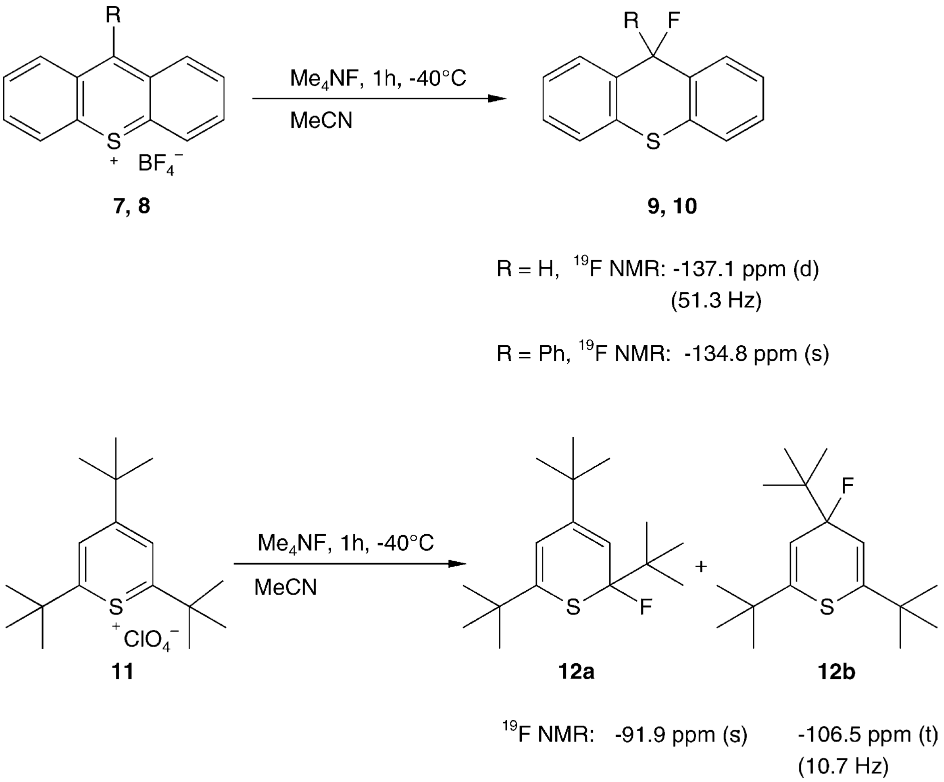
We reacted unsubstituted thiopyrylium tetrafluoroborate (**1**) with strong basic F^- (naked F^-) as in $Me_4N^+F^-$ at −40 °C in acetonitrile and followed the reaction solution at low temperatures with NMR spectroscopy. No S–F products were detectable. Products are 2-fluoro-2H-thiopyrane (**3a**), and 4-fluoro-4H-thiopyrane (**3b**) in the molar ratio 93:7 (Scheme 2).

The same reaction at −90 °C in propionitrile gives the same result, **3a**:**3b** = 94:6 (Scheme 2).

The reaction of thiopyrylium iodide (**2**) with AgF at −40 °C in acetonitrile yields **3a** and **3b** in the same ratio



Scheme 2. Reactions of thiopyrylium and benzothiopyrylium salts with F^-.



Scheme 3. Reactions of thioxanthylium and 2,4,6-tri-*tert*-butyl-thiopyrylium salts with F^-.

(93:7) as the reaction of **1** with $Me_4N^+F^-$, again no S–F product was detectable. The relative concentration of 2-fluoro/4-fluoro isomers corresponds to the thermodynamic product control favoring the 2H-thiopyranes, as has been observed in numerous reaction of thiopyrylium salts (review to the chemistry of thiopyrans [1,17,18]) and is also predicted by ab initio calculations discussed above (Fig. 2).

NMR data of **3a** and **3b** are assigned in detail (see Section 4), e.g. doublets in the ^{19}F NMR spectrum with $J = 54$ Hz are typical for geminal $^{19}F,^{1}H$ coupling constants [19]. A complete assignment of the ^{13}C resonances of **3a** is possible by comparison with 2-MeO-2H-thiopyrane (**4**) [20,21], which shows similar ^{1}H and ^{13}C spectra.

If the 2 position is protected as in the 1-benzothiopyrylium salt (**5**), again a mixture of 2-fluoro-2H-1-benzothiopyrane (**6a**) with very little 4-fluoro-4H-1-benzothiopyrane (**6b**) is obtained, **6a**:**6b** = 97:3 (Scheme 2).

A further protection of the 2 and 4 positions in the thiopyrylium ring is employed in the thioxanthylium and 9-phenyl-thioxanthylium tetrafluoroborate (**7** and **8**). Both salts react with $Me_4N^+F^-$ in acetonitrile at −40 °C completely to the corresponding 9-fluoro-9H derivatives (**9** and **10**) (Scheme 3). So double blocking of the 2 position only directs the F^- attack into the 4-position that cannot be prevented even by the phenyl substitution.

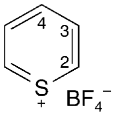
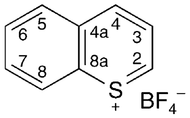
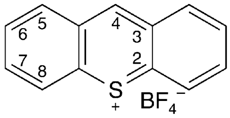
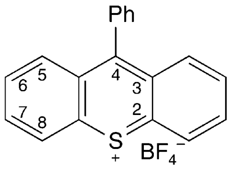
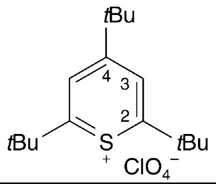
Blocking of the 2 and 4 positions in the thiopyrylium ring has been tried also by strong steric protection, as in 2,4,6-tri-*tert*-butyl thiopyrylium perchlorate (**11**). Reacting this salt with $Me_4N^+F^-$ in acetonitrile at −40 °C gives two ^{19}F NMR signals (**12a**:**12b** = 70:30) in the same region as in the previously mentioned fluorothiopyranes, and no indication for a S–F intermediate (Scheme 3).

In summary no attack of the F^- ion on the S atom in the $C_5H_5S^+$ ring has been observed. If such an intermediate is formed at all in the first step, it rearranges rapidly into the 2-fluoro-2H-thiopyrane which is calculated to be 20 kcal mol^{-1} more stable. More likely is the direct attack on the carbon atom of $C_5H_5S^+$, especially at the electron deficient positions C-2 and C-4. ^{13}C NMR chemical shifts can be interpreted as a function of electron density in such ring systems. (For the NMR spectroscopy of S-containing cyclic 6π cations and tropylium salts, see [22].) Therefore we have measured the ^{13}C NMR spectra of the compounds **5**, **7**, **8** and **11** (see Table 2). The assignment for **5**, **7**, and **8** is based on combinations of $^{1}H,^{1}H$-COSY, $^{13}C,^{1}H$-COSY, and $^{1}H,^{13}C$-HMBC measurements.

3.2. Attempts to synthesize acyclic precursors carrying a SF_5 group

According to Scheme 1 (case a), for the (*Z*)-stereoselective double bond formation a 2-pentafluorothioethyl triphenylphosphonium salt and also a pentafluorothio acetaldehyde could be used (Wittig reaction). C–C bond formation according to Scheme 1 (case b), could be carried out by penta-

Table 2
^{13}C NMR chemical shifts (ppm) of the thiopyrylium salts **1**, **5**, **7**, **8**, **11** (CD_3CN)

Compound	Structure	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
1 [2]		158.78	138.25	150.80						
5		164.42	131.48	154.94	136.14	134.86	136.61	129.58	133.78	146.00
7		149.38	130.73	162.01	138.20	132.29	139.83	128.29		
8[a]		149.43	131.41	172.53	136.50	132.08	138.60	128.66		
11[b]		185.71	131.00	177.49						

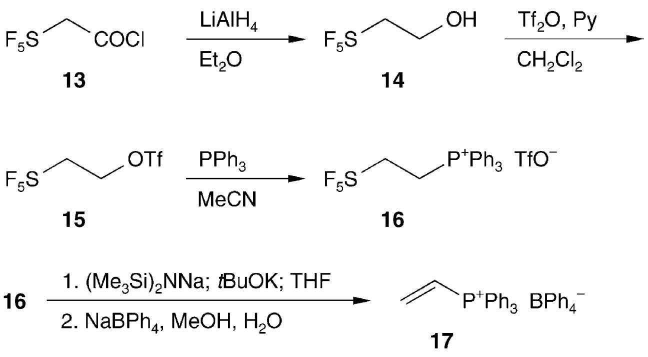
[a] Ph: 135.69 (*i*), 130.48 (*o*), 129.79 (*m*), 131.68 (*p*).

[b] 2,6-*t*Bu: 31.23 (CH_3), 42.87; 4-*t*Bu: 30.32 (CH_3), 40.17.

fluorothio ethyne as unsaturated component (review of compounds with SF_5 group [23]).

Photo addition of SF_5Cl on ketene delivers the acetylchloride (**13**) [24], which in turn can be reduced by $LiAlH_4$ to the alcohol (**14**) [25]. **14** is transformed by trifluoromethane sulfonic acid anhydride (Tf_2O)/pyridine according to [26] into the triflate (**15**). **15** reacts in MeCN with PPh_3 to the phosphonium salt (**16**) in high yield. Attempts failed to change **16** into the corresponding ylid by the bases $(Me_3Si)_2NNa$ or K *tert*-butylate. Deprotonation of **16** results in the complete elimination of the SF_5 group under formation of the vinyl triphenylphosphonium ion that could be isolated as tetraphenylborate (**17**) (Scheme 4).

Pentafluorothio acetaldehyde can be prepared by a tedious and very inefficient route [27,28]. Our attempts to obtain it from the acid chloride **13** with $Bu_3SnH/Pd(PPh_3)_4$ [29] or with H_2/Pd on charcoal in the presence of 2,6-dimethylpyridine [30] have been unsuccessful. By oxidizing the alcohol **14** with $n\text{Pr}_4\text{N}^+\text{RuO}_4^-$, *N*-methylmorpholin-*N*-oxide (TPAP/NMO) [31,32] or $PhI(OAc)_2$/TPAP [33] produced the aldehyde only in small amounts. Synthesis of pure pentafluorothio acetaldehyde in a preparative amount has not been possible.$F_5S–C≡CH$, prepared from $SBrF_5$ and C_2H_2 in modest yields (∼25%) [34], could not be coupled with $I–C≡C–CH_2–SiMe_3$ [35] to give $F_5S–C≡C–C≡C–CH_2–SiMe_3$ in the presence of CuI/pyrrolidine according to [36] Using Et_3N as a base also gave complete decomposition without any coupling product. *Stille* coupling avoids such basic conditions. Attempts to prepare $F_5S–C≡C–SnMe3$ with trimethyltinpyrrole [37] that could be used for the *Stille* coupling, have been unsuccessful.



Scheme 4. Attempted synthesis of triphenylphosphonium pentafluorothio ethylide.

In summary it has not been possible to obtain appropriate acyclic precursors for the preparation of the thiopyrylium-S-trifluoride.

4. Experimental

4.1. *General*

The density functional and ab initio calculations have been performed with the Gaussian program (revision A.7), and the basis sets implemented therein [38]. All given energies are corrected for zero point energies. All compounds that are not explicitly marked as transition states have no imaginary vibrational frequencies.

NMR spectra have been measured in 5 mm tubes on a JEOL JNM-LA 400 spectrometer: ^{1}H at 399.65 MHz (^{1}H reference: TMS in $CDCl_3$, $\delta = 0$), ^{13}C at 100.40 MHz (^{13}C reference: TMS in $CDCl_3$, $\delta = 0$, CD_3CN: $\delta = 1.30$, CH_3CN: $\delta = 0.8$ [39]), ^{19}F at 376.00 MHz (^{19}F reference: $CFCl_3$ in $CDCl_3$ as external, $\delta = 0$).

1 was synthesized according to [2], **5** by the sequence: thiophenol/β-bromo propionic acid → β-phenylthio propionic acid [40] → thiochromanone [40] → thiochromanol [41] → 1-benzo-2H-thiopyrane [42]. The latter was reacted with $Ph_3C^+BF_4^-$ in acetonitrile according to [2,43] giving **5**. Preparation of the thioxanthylium salts **7** and **8** started with thioxanthon: reduction to thioxanthol by $NaBH_4$ [44] or to 9-phenyl thioxanthol by reaction with PhLi [45]. Preparation of **11** was carried out according to [46] starting with pinacolone and pivalaldehyde [47,48]. Anhydrous $Me_4N^+F^-$ was obtained by a drying procedure of the tetrahydrate in high vacuum (d, 130 °C) [49]. Preparations of **13** [24], **14** [25], $F_5S\text{–}C{\equiv}CH$ [34], $I\text{–}C{\equiv}C\text{–}CH_2\text{\_}SiMe_3$ [35], and trimethyltin-pyrrole [37] followed known procedures.

4.2. *Preparation of the thioxanthylium tetrafluoroborates (**7** and **8**)*

A solution of 25 mmol thioxanthole (5.36 g) or 9-phenyl thioxanthole (7.26 g) in 100 ml dry diethyl ether, containing also 5.1 g (50 mmol) acetanhydride, was cooled under argon to −78 °C. Into the stirred solution 54% $HBF_4{\cdot}Et_2O$ (10.2 ml, 75 mmol) was injected. Warming to room temperature, filtration of the precipitated dark red crystals under argon, washing with ether and recrystallization from acetonitrile in the presence of 0.5 ml $HBF_4{\cdot}Et_2O$ ether by slow action of 100 ml ether gave the desired products. Yield **7**: 6.6 g (93%), mp 172–176 °C (dec.), **8**: 7.76 g (85%), mp 186–190 °C.

4.3. *Reaction of thiopyrylium salts **1**, **5**, **7**, **8**, and **11** with $Me_4N^+F^-$*

A well dried tetrafluoroethene-perfluorovinylether copolymer (PFA) tube of 12 mm diameter, equipped with a metal valve, was filled with 1 mmol of the thiopyrylium salt and 1.2 mmol $Me_4N^+F^-$ (112 mg). At a high vacuum line 4 ml dry CH_3CN were condensed in at −196 °C, followed by stirring at −40 °C for 1 h. By external Ar pressure a part of the reaction solution was transferred into a 4 mm PFA tube up to 5 cm length. The 4 mm PFA tube was placed into a 5 mm NMR glass tube which contained a small amount acetone d_6. The samples were measured in the NMR spectrometer at −40 °C.

In a similar fashion thiopyrylium salt **1** was reacted with $Me_4N^+F^-$ in propionitrile (4 ml) for 3 h at −90 °C, NMR measurement at −90 °C. Thiopyrylium salt **2** (1 mmol, 224 mg) was reacted with AgF (1.2 mmol, 152 mg) in MeCN for 3 h at −40 °C.

The ring positions for the ^{13}C NMR assignment correspond with Table 2.

3a: ^{19}F NMR (MeCN) δ: −104.60 (dd, $^{2}J_{FH} = 54.7$ Hz, $^{3}J_{FH} = 3.9$ Hz); ^{13}C NMR (MeCN) δ: 85.90 (d, $^{1}J_{FC} = 213.4$ Hz, C-2), 112.89 (d, $^{2}J_{FC} = 25.6$ Hz, C-3), 127.77 (d, $^{3}J_{FC} = 4.3$ Hz, C-4), 118.83 (d, $^{4}J_{FC} = 1.9$ Hz, C-5), 120.15 (d, $^{5}J_{FC} = 1.7$ Hz, C-6).

3b: ^{19}F NMR (MeCN) δ: −108.29 (d, $^{2}J_{FH} = 53.5$ Hz).

6a: ^{19}F NMR (MeCN) δ: −113.50 (dd, $^{2}J_{FH} = 53.8$ Hz, $^{3}J_{FH} = 4.0$ Hz); ^{13}C NMR (MeCN) δ: 86.38 (d, $^{1}J_{FC} = 213.2$ Hz, C-2), 117.18 (d, $^{2}J_{FC} = 23.0$ Hz, C-3), 131.04 (d, $^{3}J_{FC} = 5.6$ Hz, C-4), 128.14 (d, $^{4}J_{FC} = 2.9$ Hz, C-4a), 127.43 (C-8a), 125.79, 126.43, 128.71, 129.46 (aromatic C-5 to C-8 without exact assignment).

6b: ^{19}F NMR (MeCN) δ: −117.30 (d, $^{2}J_{FH} = 55.2$ Hz).

9: ^{19}F NMR (MeCN) δ: −137.10 (d, $^{2}J_{FH} = 51.3$ Hz); ^{13}C NMR (MeCN) δ: 89.55 (d, $^{1}J_{FC} = 160.9$ Hz, C-4), 129.16 (d, $^{2}J_{FC} = 22.7$ Hz, C-3), 132.70 (d, $^{3}J_{FC} = 2.9$ Hz, C-2), 126.10 (d, $J_{FC} = 2.5$ Hz), 126.51 (d, $J_{FC} = 2.1$ Hz), 129.38 (d, $J_{FC} = 3.7$ Hz), 130.96 (d, $J_{FC} = 4.1$ Hz) (aromatic C-5 to C-8 without exact assignment).

10: ^{19}F NMR (MeCN) δ: −134.80 (s); ^{13}C NMR (MeCN) δ: 94.00 (d, $^{1}J_{FC} = 180.1$ Hz).

12a: ^{19}F NMR (MeCN) δ: −91.90 (s).

12b: ^{19}F NMR (MeCN) δ: −106.5 (t, $^{3}J_{FH} = 10.7$ Hz).

4.4. *2-Methoxy-2H-thiopyrane (**4**)*

A mixture of thiopyrylium salts **1** (15 mmol, 2.76 g) and 30 ml MeOH was added dropwise into a NaOMe solution in MeOH (460 mg, 20 mmol Na in 20 ml MeOH) and stirred for 30 min. Addition of 200 ml H_2O, 3× extraction with 60 ml Et_2O, washing of the organic phase with H_2O, $NaHCO_3$, and NaCl solutions and drying above Na_2SO_4 give a pure product, as shown by NMR spectrum. Yield **4**: 1.4 g (73%). ^{13}C NMR ($CDCl_3$) δ: 74.75 (C-2), 114.67 (C-3), 126.49 (C-4), 119.28 (C-5), 120.88 (C-6), 51.86 (MeO).

4.5. *2-(Pentafluorothio)ethyl triflate (**15**)*

A solution of 2-pentafluorothio ethanol **14** (8.6 g, 50 mmol) and 4 g (50 mmol) pyridine in 15 ml dry CH_2Cl_2

was added dropwise at 0 °C within 45 min to a stirred solution of trifluoromethane sulfonic acid anhydride (Tf_2O) in 50 ml CH_2Cl_2. Stirring for additional 1 h, washing with 200 ml ice water, drying over Na_2SO_4, pumping off the CH_2Cl_2 in vacuum and distillation in vacuum through a short vigreux column at 75 °C/20 mbar afforded 12.96 g (85%) **15**.

^{19}F NMR ($CDCl_3$) δ: 65.48 (F_{eq}), 79.52 (F_{ax}, $^2J_{FF} = 145.9$ Hz, AB_4 spectrum [50]), −75.61 (CF_3). ^{13}C NMR ($CDCl_3$) δ: 67.66 (qi, $^2J_{FC} = 17.2$ Hz, CH_2–SF_5), 69.55 (qi, $^3J_{FC} = 5.2$ Hz, CH_2–O), 118.58 ($^1J_{FC} = 319.2$ Hz, CF_3).

4.6. 2-Pentafluorothioethyl triphenylphosphonium triflate (*16*)

An amount of 9.1 g (30 mmol) triflate **15** and 7.9 g (30 mmol) triphenylphosphane were stirred for 3 h at 50 °C in 30 ml dry CH_3CN. Precipitated crystals after treatment with 300 ml of dry ether were collected and washed with 100 ml Et_2O, yield 14.73 g (87%) **16**, mp 165–167 °C.

^{19}F NMR (CD_3CN) δ: 64.44 (F_{eq}), 81.19 (F_{ax}, $^2J_{FF} = 145.7$ Hz, AB_4 spectrum), −79.48 (CF_3); ^{31}P NMR (CD_3CN) δ: 24.0. ^{13}C NMR (CD_3CN) δ: 20.98 (d, qi, $^1J_{PC} = 53.8$ Hz, $^3J_{FC} = 4.8$ Hz, CH_2–P), 64.77 (qi, $^2J_{FC} = 17.0$ Hz, CH_2–SF_5), 117.61 (d, $^1J_{PC} = 87.4$ Hz, *i*-C), 131.64 (d, $^3J_{PC} = 12.8$ Hz, *m*-C), 134.87 (d, $^2J_{PC} = 10.5$ Hz, *o*-C), 136.75 (d, $^4J_{PC} = 3.1$ Hz, *p*-C), 122.21 (q, $^1J_{FC} = 321.2$ Hz, CF_3), assignment of P-Ph (see [51]).

4.7. Reaction of triphenylphosphonium salt (*16*) with bases

A suspension of 2.26 g (4 mmol) phosphonium salt (**16**) in 20 ml THF was added dropwise at −20 °C under argon into a stirred solution of $(Me_3Si)_2NNa$ (0.81 g, 4 mmol) in 5 ml THF. Stirring for additional 2 h during warming to room temperature, was followed by pumping off the solvent and dissolution in $MeOH/H_2O$ (10 ml/40 ml) and filtration. To this stirred solution was added dropwise a solution of $NaBPh_4$ (4 mmol, 1.37 g) in H_2O (20 ml). The precipitate was collected, washed with 40 ml H_2O and 80 ml hexane and dried in vacuum. The crude product was recrystallized from boiling CH_3CN (12 ml). For completion of the crystallization 100 ml Et_2O was added, and the colorless salt is filtered off, yield 0.9 g (37%) of **17**; if *t*BuOK was used as a base, the yield of **17** was 0.64 g (26%), mp 224–226 °C (dec.).

^{13}C NMR (CD_3CN) δ: 118.89 (d, $^1J_{PC} = 82.9$ Hz, CH_2=*C*H–P), 146.17 (s, *C*H_2=CH–P), 118.29 (d, $^1J_{PC} = 90.7$ Hz, *i*-C, P-Ph), 131.34 (d, $^3J_{PC} = 13.0$ Hz, *m*-C, P-Ph), 135.06 (d, $^2J_{PC} = 10.7$ Hz, *o*-C, P-Ph), 136.39 (d, $^4J_{PC} = 2.9$ Hz, *p*-C, P-Ph), 122.77 (s, *p*-C, B-Ph), 126.57 (q, $^3J_{CB} = 2.8$ Hz, *m*-C, B-Ph), 136.74 (q, $^2J_{CB} = 1.4$ Hz, *o*-C, B-Ph), 164.77 (q, $^1J_{CB} = 49.3$ Hz, *i*-C, B-Ph), assignment of CH_2=CH–PPh_3^+ (see [51,52]) and BPh_4^- (see [51]). ^{31}P NMR (CD_3CN) δ: 20.75.

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