Cyclic Aryleneazachalcogenes, X[◇]

Synthesis, Molecular Structure and Photoelectron Spectrum of 6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine and Attempted Syntheses of Related Larger Size Heterocycles[1]

Irina Yu. Bagryanskaya[a], Hans Bock*[c], Yuri V. Gatilov[a], Alois Haas*[b], Makhmut M. Shakirov[a], Bahman Solouki[c], and Andrey V. Zibarev*[a]

Institute of Organic Chemistry, Russian Academy of Sciences[a],
630090 Novosibirsk, Russia

Institute of Inorganic Chemistry II, Ruhr University in Bochum[b],
Universitätsstraße 150, D-44780 Bochum, Germany

Institute of Inorganic Chemistry, J. W. Goethe University[c],
Marie-Curie-Straße 11, D-60439 Frankfurt am Main, Germany

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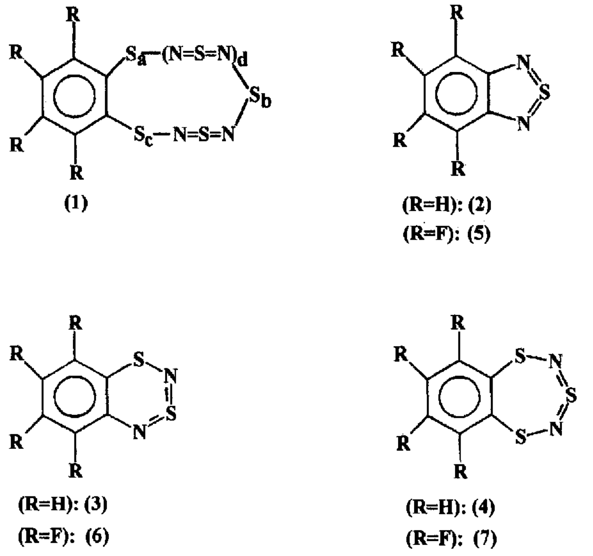
The 14π-electron title compound **7** has been synthesized by two different ring-closure approaches. Its structure has been determined by X-ray diffraction to be planar within ±0.018 Å. The He(I) photoelectron spectrum of the title compound is assigned by Koopmans' correlation with PM3 eigenvalues based on the structural data, and by the π-perfluoro effect observed. The π-system can be rationalized by heteroatom first-order perturbation, which reduces the cyclic π-delocalization. Replacement of the four fluorine substituents by hydrogen affects neither the long-wavelength absorption band in the UV/Vis spectrum nor the δ^{15}N shift in the ^{15}N-NMR spectrum. The synthesis of 20π-electron heterocycles related to the title compound has been attempted.

Cyclic aryleneazathienes **1** (Scheme 1) contain π-heterocycles composed of one π_{CC} bond and chains of N=S=N and N−S−N subunits, which are planar with appropriate ring sizes (indices a, b, c and d), and are of interest due to their varying π-delocalization. Known derivatives comprise 2,1,3-benzothiadiazole **2** with 10 π-electrons[2], 1,3,2,4-benzodithiadiazine **3**[3], and 1,3,5,2,4-benzotrithiadiazepine **4** with 14 π-electrons[3,4] as well as the tetrafluoro derivatives of **2** and **3**, namely **5** and **6**[5,6] (Scheme 1). The latter are useful for the assignment of π-ionizations in the He(I) photoelectron spectra[7−10] by the well-known perfluoro effect[8,9,15a].

Of interest are efforts to prepare related heterocycles of larger size, in particular with 20 π-electrons (**8** or **9**; Scheme 2).

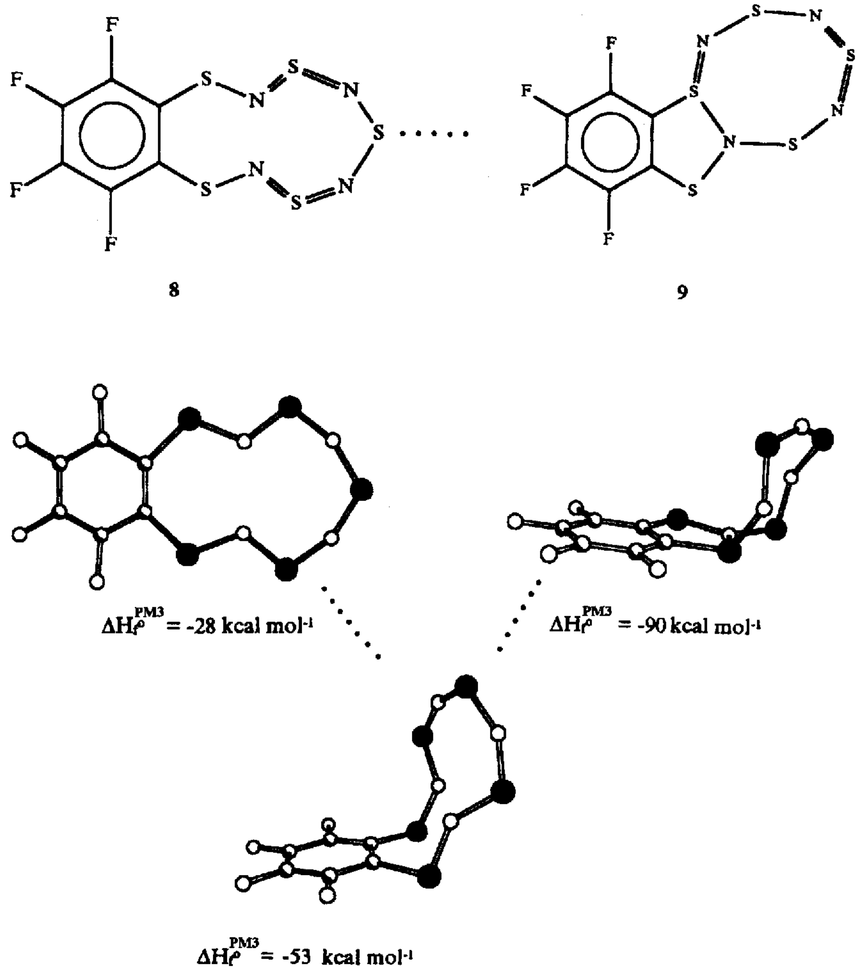
In contrast to the planar benzoheterocycles **2**−**7** of this series (Scheme 1), the structure of a derivative containing an eleven-membered ring ($C_2N_4S_5$), with $3N - 6 = 3 \times 11 - 6 = 27$ degrees of freedom, is difficult to predict. According to PM3 calculations (Scheme 2 and Experimental Section), a planar structure seems to be a local minimum on the corresponding hypersurface. However, within a simplifying MO model[11a], in which π*-levels would be occupied in the molecular ground state, some thermodynamic destabilization might be expected, and, in addition to non-planar conformations of **8** with limited π-delocalization, the formation of a transannular σ(S−N) bond analogous to the known bicyclic structure of cyclopenta(azathienium)

Scheme 1



[◇] Part IX: Ref.[1].

Scheme 2



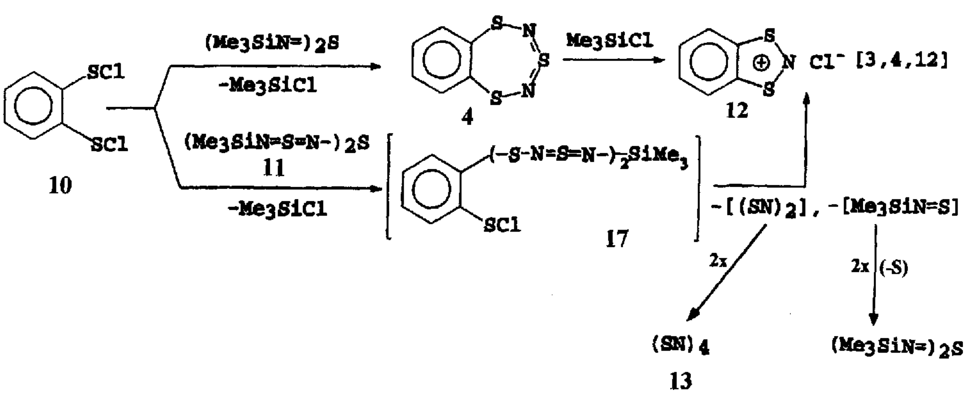
(SN)$_5^+$[11], might be especially favourable. The approximate PM3 calculations (Scheme 2) would support these assumptions for the structure of **9** with 20 π-electrons (Scheme 2).

In addition to attempts to prepare larger-size benzothiaazepines (Schemes 3 and 4), the synthesis, molecular structure and photoelectron spectrum of 6,7,8,9-tetrafluoro-1,3,5,2,4-benzotrithiadiazepine (**7**; Scheme 1) is reported herein.

Results and Discussion

The condensation of benzene-1,2-disulfenyl dichloride (**10**) with $(Me_3SiN{=})_2S$ was used to prepare **4**[3,4]. The analogous condensation with $(Me_3SiN{=}S{=}N{-})_2S$ (**11**) afforded 1,3,2-benzodithiazolium chloride **12** and cyclotetra(azathiene) (**13**) (Scheme 3) rather than the expected parent system of **8**. The salt **12** was formed during the synthesis

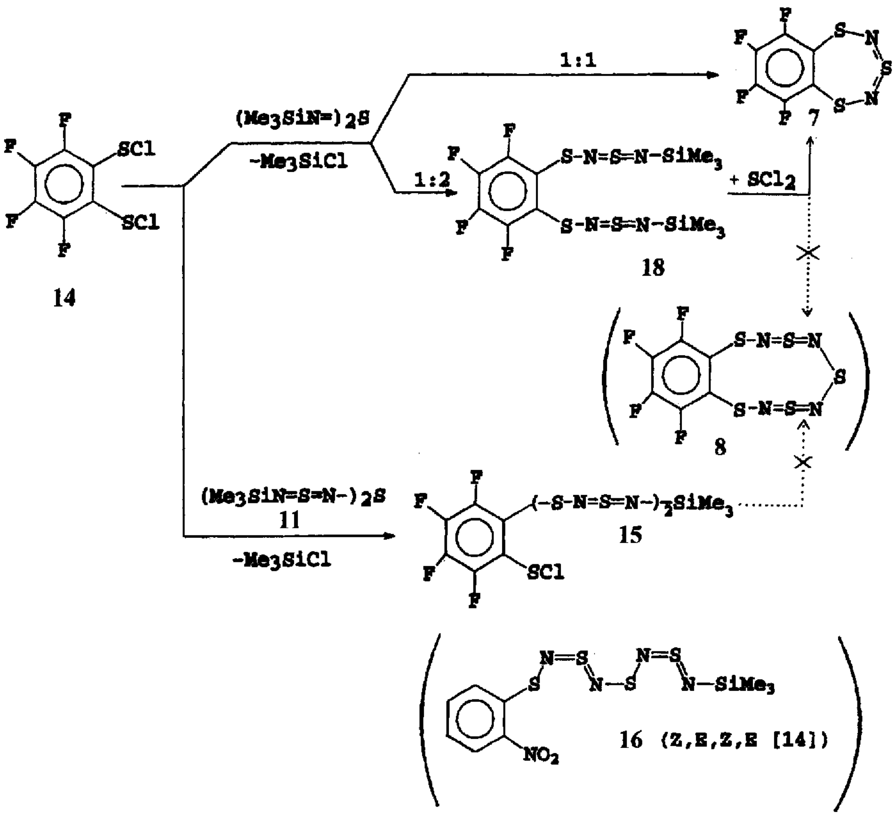
Scheme 3



of **4**, as a byproduct from a reaction of **4** with Me_3SiCl (Scheme 3)[4,12].

The formation of the benzodithiazolium salt **12** was suppressed on going from **10** to its tetrafluoro derivative **14** (Scheme 4). The reaction of **14** with $(Me_3SiN{=})_2S$ yielded only **7** (Scheme 4) without any evidence for the formation of the polyfluorinated benzodithiazolium salt **12** (Scheme 3).

Scheme 4



In the reaction of **14** with $(Me_3SiN{=}S{=}N{-})_2S$, however, an unstable intermediate was formed, for which the available data suggest structure **15** and which does not undergo ring-closure to **8**. To form this ring, the planar *E*,*Z*,*Z*,*E* configuration of **11**[13] should be rather favourable, but in solution presumably a *Z*,*E*,*Z*,*E* configuration of **15**, with distant SCl and $NSiMe_3$ groups dominates, analogous to that determined for the related compounds **16**[14] (Scheme 4).

Formation of **8** might also have been expected from the reaction of compound **18** (Scheme 4) with SCl_2; however, the smaller ring-size heterocycle **7** turned out to be the major reaction product.

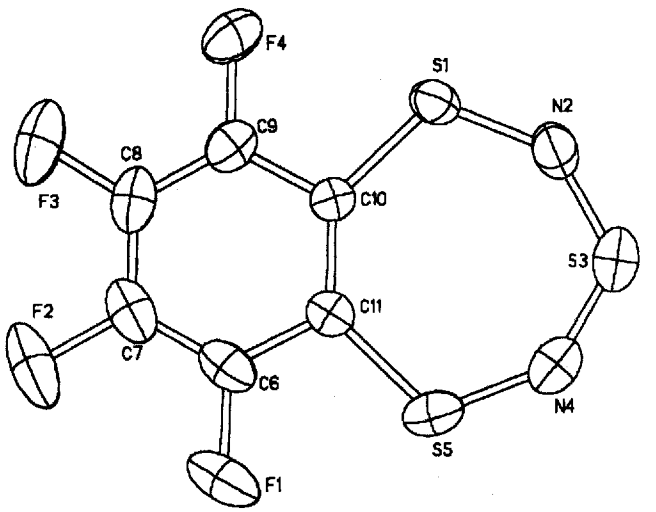
The structure of 6,7,8,9-tetrafluoro-1,3,5,2,4-benzotrithiadiazepine was determined by X-ray diffraction analysis (Figure 1 and Table 1). The molecule was found to be planar within ±0.018 Å, with the largest deviations of N2, S3 and N4 from the plane of the six-membered ring amounting to −0.047(9), −0.062(9) and −0.044(9) Å (numbering cf. Figure 1). In the six-membered heterocyclic derivative **6** the corresponding deviations of S and N centers are larger, amounting to 0.132(1) and 0.165(3) Å[6], respectively.

The reproduction of the experimentally determined bond lengths by PM3-calculated ones is remarkable (Table 1); the largest deviations result for the S−N bonds.

The He(I) photoelectron spectrum of **7** is well-resolved and even exhibits vibrational fine structures (Figure 2). Its assignment by Koopmans' correlation with PM3 eigenvalues, calculated on the basis of the structural data (Table 2), seems to be straightforward, and, of the respective π-molecular orbitals, three show dominant contributions of the SN-heterocyclic ring (Figure 3). The assignment clearly suggests that in **7** both the six- and seven-membered rings form one π-electron system. The first-order perturbation exerted by the hetero centers according to the respective nuclear charges, however, restricts the π-electron delocalization around the molecular perimeter to some extent. This effect[10] is typical for all compounds of type **1** studied to date[8−10].

A detailed analysis of the He(I) PE spectrum of the title compound reveals interesting facts: The first vertical ionization energy of **7** is lower than that of 1,2,3,4-tetrafluorobenzene at IE_1^v = 9.8 eV[16], and can be rationalized within a MO model by the rather large contributions of the sulfur centers to the molecular orbital π_1 (Figure 3). The 0.37 eV shift of the first band relative to the hydrogen derivative **4** (Table 4) can be considered to be a manifestation of the

Figure 1. Molecular structure of 6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine (7)[a]



[a] Selected bond lengths [Å] and bond angles [°]: C10−S1 1.737(4), S1−N2 1.604(4), N2−S3 1.531(5), S3−N4 1.519(5), N4−S5 1.603(5), S5−C11 1.746(5), C11−C10 1.407(6), av. C−F 1.349, av. C−C 1.382; C10−S1−N2 115.5(2), S1−N2−S3 140.3(3), N2−S3−N4 120.7(2), S3−N4−S5 141.1(3), N4−S5−C11 115.3(2), S1−C10−C11 134.1(3), C10−C11−S5 132.9(3).

perfluoro π-effect in this type of heterocycle, since the coefficients of the adjacent carbon centers (Figure 3) are either zero or rather small (cf. data for compounds **2** and **5** or **3** and **6**[8−10]). The vibrational structure of the first band (Table 2) is possibly due to S−N bond stretching vibrations corresponding to bands at ṽ = 1260, 1248 and 1175 cm^{-1} in the IR spectrum of **7**.

Table 1. Comparison of selected bond lengths [Å] in 1,3,5,2,4-benzotrithiadiazepine (**4**) and 6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine (**7**) from experimental X-ray and calculated PM3 data (numbering cf. Figure 1)

	X-ray structure		PM3 (C_{2v})	
	7	**4**[4a]	**7**	**4**
C10-S1	1.742	1.732	1.76	1.75
S1-N2	1.603	1.609	1.66	1.67
N2-S3	1.525	1.538	1.60	1.60
C7-C8	1.363	1.396	1.41	1.40
C8-C9	1.353	1.349	1.40	1.37
C9-C10	1.409	1.420	1.43	1.42
C10-C11	1.407	1.387	1.41	1.40

The second vertical ionization of **7** corresponds to the π_2 MO with large contributions from the S^{IV} as well as the S^{II} centers (Figures 2 and 3). The band shift relative to the parent hydrogen derivative **4** amounts to 0.46 eV (Table 2). The vibrational structure of the second band (Table 2) possibly resembles C=C bond stretching vibrations characteristic of polyfluorobenzene derivatives, while the IR spectrum of **7** exhibits a band of medium intensity at ṽ = 1634 cm^{-1} and very strong one at ṽ = 1513 cm^{-1}. This vibrational assignment would support some carbocycle participation in the corresponding radical cation state in accordance with the PM3 molecular orbital π_2 (Figure 3).

The third and fourth vertical ionization energies of **7**, IE^v_3 and IE^v_4, overlap to form a double-intensity band with a maximum at 10.3 eV and a shoulder at 10.1 eV, and according to the assignment (Table 2) represent the π_3 and σ_N

Figure 2. He(I) photoelectron spectrum of 6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine (7)

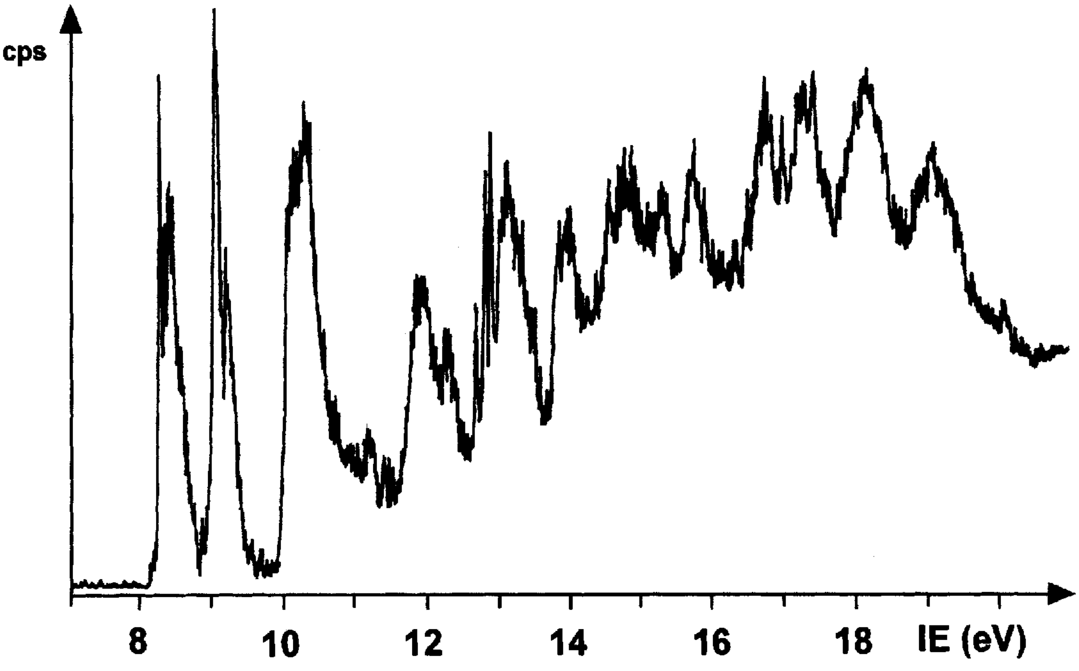
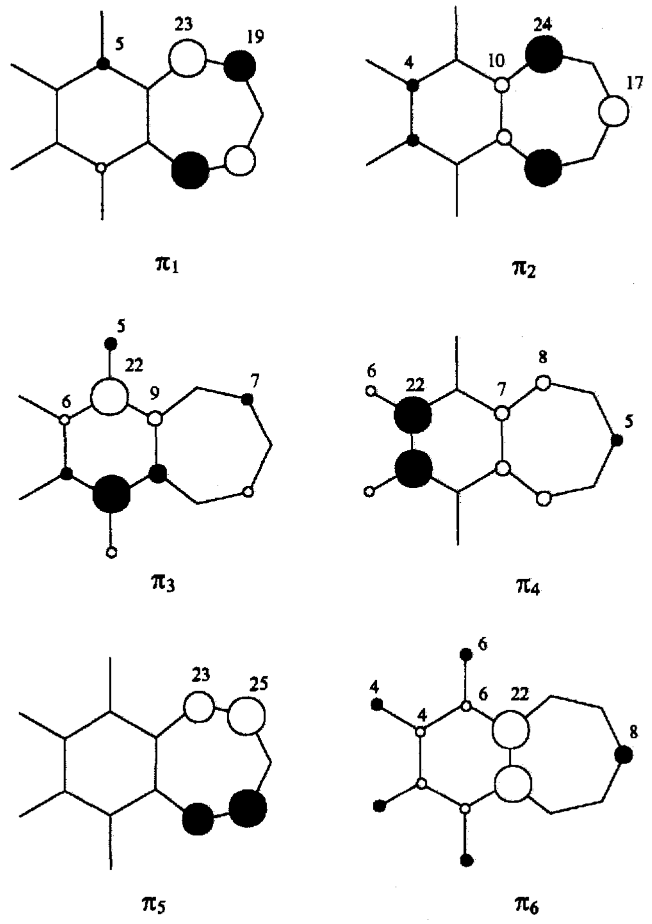


Table 2. Experimental vertical ionization energies IE_i^v and vibrational fine structures ν, as well as assignment by Koopmans' correlation with PM3 eigenvalues for tetrafluorobenzotrithiadiazepine **7**; for comparison, the PE-spectroscopic data of the parent compounds **4** are listed

IE_i^v (eV)		$\tilde{\nu}$ (cm^{-1})		$-\varepsilon_i$ (eV)		$(\Phi_i)^{-1}$
7	**4**[7]	**7**	**4**[7]	**7**		
8.25	7.88	1200	1070	8.84	π	π_1
9.0	8.54	1600		9.60	π	π_2
~ 10.1 (sh)	~ 9.60 (sh)			11.05	π	π_3
10.3	9.87			11.12	σ	σ_N
11.2	11.0			11.61	σ	(σ)
11.9	11.4			11.99	π	(π)
12.3	12.5			13.12	σ	(σ)
12.88		1120		13.55	σ	(π)
13.06	13.0 (sh)			13.72	π	
13.9	14.0			14.39	π	

Figure 3. Highest occupied π-MOs of 6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine from PM3 calculations; the numbers denote the contributions (%) of a given AO in the respective MO (contributions of less than 4% are neglected)



radical cation states. The radical cation state $\tilde{B}$ ($^2A_2$) should possess a large carbocycle component, which correlates with the benzene π_s (e_{1g}) orbital, while the σ_N one shows predominant N contributions. Due to the overlapping of the bands, their shift from **4** to **7**, i.e. the perfluoro effect (π versus σ) loses its diagnostic significance, in contrast to the situation with the pair of compounds **3** and **6** (Scheme 3)[9].

For the other radical cation states of **7**, a definite sequence is difficult to establish. It is worthwhile to note, however, that the well-resolved vibrational structure of the band at 12.88 eV (Table 2) presumably originates from a π-state, which may correlate to a carbocycle-localized π_6 MO (Figure 3): The frequency observed is typical for C–F bond stretching vibrations, and the IR spectrum of **7** exhibits a band of medium intensity at $\tilde{\nu}$ = 1175 and intense bands at $\tilde{\nu}$ = 1100 and 1018 cm^{-1}. Alternatively, another possibility would be an assignment to the azathiene chain-localized π_5 MO (Figure 3) since the frequency is very similar to that of the first band in the photoelectron spectrum (Table 2).

Comparison of the UV/Vis spectra of **7** and **4** shows that the complete replacement of hydrogen in **4** by fluorine has virtually no effect on the position of the long-wavelength absorption-band maximum (**4**: λ = 384 nm[3]; **7**: λ = 380 nm; Table 3). This indicates that the electronic π-π* transition responsible for the yellow colour of both **7** and **4** (see[1] and references cited therein) should originate in the azathiene chain.

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Experimental Section

The ^1H- and ^{19}F-NMR spectra were recorded with a Bruker WP-200SY spectrometer at frequencies of 200 and 188.28 MHz, respectively, with internal standards TMS and C_6F_6. The natural-abundance ^{15}N-NMR spectra were recorded with a Bruker AM-400 spectrometer at a frequency of 40.55 MHz with external standards NH_3 (liqu.). The ^{15}N shifts in **4** and **7** are very similar (**4**: δ = 248.8[1], 243.2; Table 3). Comparison with data from other compounds shows a regular increase of the ^{15}N nuclei magnetic shielding in compounds **2**, **3** and **4**[1] whereas for the fluoro derivatives **5**, **6** and **7** this effect is less prominent (ref.[1] and Table 3).

Table 3. NMR- and UV/Vis-spectral data of compounds

	NMR[a], δ			UV/Vis[b], λ_{max} (nm) (log ε)
	^1H	^{15}N	^{19}F	
7		243.2[c]	30.4, 2.6	380 (3.64)
14			41.4, 16.5	
15			30.1, 28.2, 15.9, 7.9	
18	0.31		34.0, 10.7	355 (4.28)

[a] Solvents: ^1H: CCl_4; ^{15}N: $C_6H_6/CDCl_3$ (3:1); ^{19}F: **7**: $C_6H_6/CDCl_3$ (3:1); **14**, **18**: CCl_4; **15**: $CDCl_3$. – [b] In heptane. – [c] d, J = 2.1 Hz; for $\delta^{15}N$ of **2**–**6**, see Ref.[1].

The mass spectra were recorded using a Finnigan MAT MS-8200 spectrometer (EI, 70 eV). The UV/Vis spectra were obtained with a Specord M40 spectrophotometer and IR spectra were recorded with a Specord M80 instrument.

The He(I) photoelectron spectrum was recorded on a Leybold Heraeus UPG 200 spectrometer equipped with a heated inlet system at 70 °C and calibrated by the $^2P_{3/2}$ ionizations of Xe and Ar.

Table 4. Crystal and refinement data of 6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine (7)[a]

Formula	$C_6F_4N_2S_3$
M	272.26
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.506(2)
b (Å)	3.9372(8)
c (Å)	19.910 (3)
β (°)	96.62(2)
V(Å^3)	895.9(3)
Z	4
D_c (g cm^{-3})	2.018
μ (cm^{-1})	79.41
F(000)	536
Crystal size (mm)	0.14 x 0.3 x 0.5
Scan mode	θ-2θ
θ range (°)	3-60
Measured reflections	1340
Transmission range	0.157 - 0.416
Final R, wR_2 (all data)	0.0635, 0.1415
Goodness of fit	1.056

[a] Atomic coordinates, thermal parameters, bond lengths, and bond angles have been decomposited with the Cambridge Crystallographic Data Centre.

The X-ray structure determination (Table 4) was carried out with a Syntex $P2_1$ diffractometer using Cu-K_α radiation with a graphite monochromator. A correction for systematic intensity drop as well as an analytical correction for absorption were made using the SHELX-76 program. The structure was solved by direct methods using the SHELX-86 program and refined by the least-squares method in the full-matrix anisotropic approximation using the SHELXL-93 program.

The PM3 calculations were performed with full geometry optimization unless otherwise indicated using both the MNDO-92[17] as well as the MOPAC (Version 6.0) programs[18].

Syntheses were carried out under argon and in absolute solvents (except for **14**). The reagents were added dropwise to the stirred solutions, and the solvents were distilled off at reduced pressure. The physical and analytical data for compounds synthesized are summarized in Tables 3 and 5.

Table 5. Characterization of the compounds

	Mp(°C), Bp (°C/Torr)	Formula[a]	Found (%) (Calculated) C	Cl	F	N	S
7	89-90	$C_6F_4N_2S_3$	26.39		28.00	10.18	35.41
			(26.47		27.94	10.29	35.29)
14	108-109/5	$C_6Cl_2F_4S_2$	25.52	25.14	26.78		22.53
			(25.44	25.09	26.86		22.61)
15	85-86 (decomp.)	$C_9H_9ClF_4N_4S_5Si$		7.45			
				(7.51)			
18[b]	49-50	$C_{12}H_{18}F_4N_4S_4Si_2$	30.02		16.05	11.77	26.92
			(30.13		15.90	11.72	26.78)

[a] M^+, m/z, measured (calculated): **7**, 271.9160 (271.9160); **18**, 477.9903 (477.9889). – [b] H (%); found (calculated): 3.50 (3.77).

3,4,5,6-Tetrafluoro-1,2-benzenedisulfenyl Dichloride (**14**): An excess of Cl_2 was passed through a solution of 4.28 g (0.02 mol) of 1,2-benzenedithiole[19] in 50 ml of CCl_4 at 20°C. The solvent was evaporated and the residue was distilled in vacuo. Compound **14** was obtained as a red oil (4.70 g, 83%).

6,7,8,9-Tetrafluoro-1,3,5,2,4-benzotrithiadiazepine (**7**) *and 1,2,3,4-Tetrafluoro-5,6-bis(1-trimethylsilyl-2,4-dithia-1,3-diaza-1,2-butadien-4-yl)benzene* (**18**): (a) Solutions of 2.83 g (0.01 mol) of **14** and 2.06 g (0.01 mol) of $(Me_3SiN{=})_2S$[20], each in 35 ml of CH_2Cl_2, were slowly mixed by adding them dropwise to 200 ml of CH_2Cl_2 at 20°C, over a period of 4 h. After a further 2 h, the solvent was distilled off, the residue was sublimied in vacuo and recrystallized from hexane. Compound **7** was isolated as transparent, yellow needles (1.8 g, 66%). – IR (KBr, ṽ, cm^{-1}): 1634 m, 1513 vs, 1378 vs, 1365 s, 1318 m, 1260 m, 1248 m, 1175 m, 1100 vs, 1018 vs, 780 s, 645 s, 575 s, 390 m (weak bands have been omitted).

(b) To a solution of 6.18 g (0.03 mol) of $(Me_3SiN{=})_2S$[20] in 10 ml of CH_2Cl_2 maintained at −50°C, a solution of 0.85 g (0.003 mol) of **14** in 10 ml of CH_2Cl_2 was added over a period of 30 min. After 1 h, the temperature was raised to 20°C. After 16 h, the solvent was evaporated, and the residue recrystallized from hexane. Compound **18** was isolated as orange-yellow crystals (0.98 g, 68%).

(c) Solutions of 0.48 g (0.001 mol) of **18** and 0.1 g (0.001 mol) of SCl_2, each in 25 ml of CH_2Cl_2, were added simultaneously to 50 ml of CH_2Cl_2 at 20°C, over a period of 2 h. After 4 d, the solvent was evaporated and the residue was recrystallized from hexane. Compound **7** was isolated as transparent, yellow needles (0.18 g, 66%).

*Reactions of ($Me_3SiN{=}S{=}N{-})_2S$ (**11**) with 1,2-Benzenedisulfenyl Dichloride* (**10**) *and 3,4,5,6-Tetrafluoro-1,2-benzenedisulfenyl Dichloride* (**14**): (a) Solutions of 1.49 g (0.005 mol) of **11**[21] and 1.06 g (0.005 mol) of **10**[22], each in 35 ml of CH_2Cl_2, were added simultaneously to 200 ml of CH_2Cl_2 at 20°C, over a period of 2.5 h. After a further 2 h, the precipitate was filtered off and recrystallized from MeCN to give 0.68 g (72%) of 1,3,2-benzodithiazolium chloride (**12**)[4,12]. The solvent was then evaporated from the filtrate and the residue was recrystallized from toluene to yield 0.12 g (26%) of cyclotetra(azathiene) (**13**)[23].

(b) Solutions of 1.49 g (0.005 mol) of **11**[21] and 1.42 g (0.005 mol) of **14**, each in 35 ml of CH_2Cl_2, were added simultaneously to 200 ml of CH_2Cl_2 at 20°C, over a period of 2 h. After 7 d, the solvent was evaporated and the residue was recrystallized from hexane/benzene (3:1). Compound **15** was isolated as air-sensitive, brown crytals (1.59 g, 68%, orange-yellow in transmitted light).

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