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Toward Molecular Wire: Synthesis, Crystal, Molecular, and π-Electronic Structure of 1,7-Bis(aryl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraenes

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ABSTRACT

The title compounds were obtained by the reaction of 1-aryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes with dichloromonosulfane or 1-aryl-4-(1-phtalimidyl)-1,3-diaza-2,4-dithia-1,2-butadienes in the presence of CsF. The latter route also afforded nonsymmetric derivatives. In contrast, the reaction of N,N,N′,N′*-tetrakis(trimethylsilyl)diaminosulfane with* S,S*-dichloro-*N*-aryliminosulfuranes (1:2) led to 1,3-bis(aryl)-1,3-diaza-2-thiaallenes and cyclotetra(azathiene). As shown by the X-ray structure analysis, the molecule of the title compound with Ar = Ph is planar, with configuration of the azathiene chain being similar to that of poly(azathiene) $(SN)_x$. The MNDO calculations indicate that most of the π-MOs of this compound, including the frontier ones, are delocalized throughout the whole molecule. The data obtained confirm the possibility of creating molecular wire for molecular electronic devices on the basis of extended acyclic azathienes. An attempt to synthesize more extended compounds than the title ones resulted in spontaneous shortening of their azathiene chains.*

INTRODUCTION

The molecular logical "NO-AND" element (NAND gate) suggested in [1] topologically represents macromolecules of the poly(azathiene) $(SN)_x$ with integrated organic groups; functionally the azathiene fragments are designed to serve as molecular wire linking the elements of a molecular electronic device (MED). However, the conducting properties of $(SN)_x$ crystals [2] should not be transferred to individual macromolecules, as has been done in [1], because of the instability of the metallic state in one-dimensional systems. Moreover, the metallic state of $(SN)_x$ is due to the presence of a certain translational symmetry element in a unit cell of a crystal [3]. Breakdown of the required symmetry on passing from $(SN)_x$ to its derivatives causes destruction of the metallic state, with all known poly(organoazathienes) [4–9] being insulators but not metals. By consideration of azathiene compounds, modelling elementary units of these polymers has shown that the conversion of $(SN)_x$ to its analogues with integrated organic groups is accompanied by substantial variations in the configuration of the sulfur–nitrogen fragment of the molecules and in the manner of their packing in a crystal [10–17]. The electronic structure of extended oligomer analogues of $(SN)_x$ is practically uninvestigated [18,19]. Thus, the applicability of azathiene chains as molecular wire has not been adequately substantiated.

The aim of our present work is the investigation of rational methods of synthesis, as well as the crystal, molecular, and π-electronic structure of 1,7-bis(aryl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraenes [20]. These model compounds contain an oligomer azathiene chain and organic groups capable of conjugation with the chain. We have also attempted synthesis of more extended azathienes.

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RESULTS AND DISCUSSION

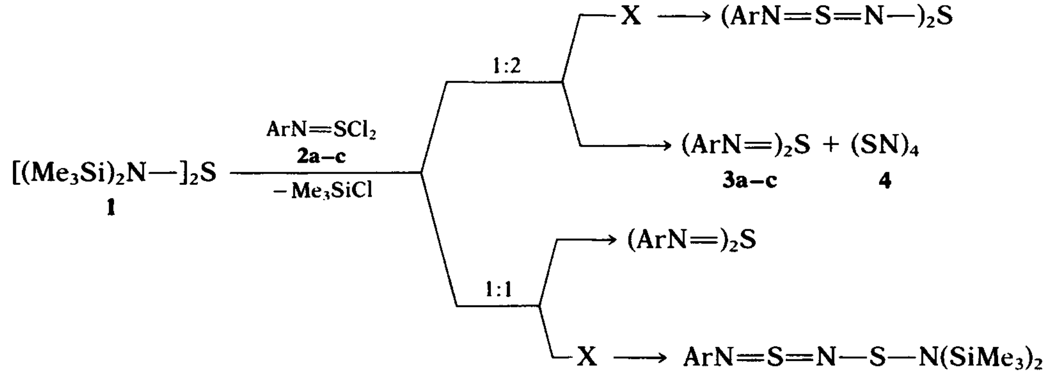
Synthesis

There are several rational approaches to the synthesis of the required compounds, for example, 1) the reaction of *S,S*-dihalo-*N*-aryliminosulfuranes with *N,N,N′,N′*-tetrakis(trimethylsilyl)diaminosulfane, which also affords nonsymmetric derivatives, and 2) the reaction of 1-aryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes with dichloromonosulfane. It appeared, however, that the main products of the reaction of *N,N,N′,N′*-tetrakis(trimethylsilyl)diaminosulfane (**1**) with *S,S*-dichloro-*N*-aryliminosulfuranes (**2**) at the reagent ratio 1:2 were 1,3-bis(aryl)-1,3-diaza-2-thiaallenes (**3**) and cyclotetra(azathiene) (**4**) (Scheme 1). Only in the case of **2a** was 1,7-bis(pentafluorophenyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (**5a**) isolated from the reaction mixture in 7% yield. At the reagent ratio 1:1, the reaction of **1** with **2** also led to **3**, whereas **4** was not formed in this case.

1-Aryl-4-trimethylsilyl-1,3-diaza-2-thiaallenes (**7**), the starting compounds in the second approach, were obtained by the reaction of *N*-sulfinylarylamines (**8**) with lithium *N,N*-bis(trimethylsilyl)amide (**9**) or 1,1,1-trimethyl-*N,N*-bis(trimethylsilyl)-stannaneamine (**10**) (Scheme 2). In general, this reaction led either to **7** or **3**, or to their mixture. Other reaction products were 1,3-bis(trimethylsilyl)-1,3-diaza-2-thiaallene (**6**) and hexamethylsilstanoxane (**12**), or hexamethyldisiloxane (**13**). The reaction of **7** with dichloromonosulfane in the ratio of 2:1 led to 1,7-bis(aryl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraenes (**5**) in high yields (Scheme 3).

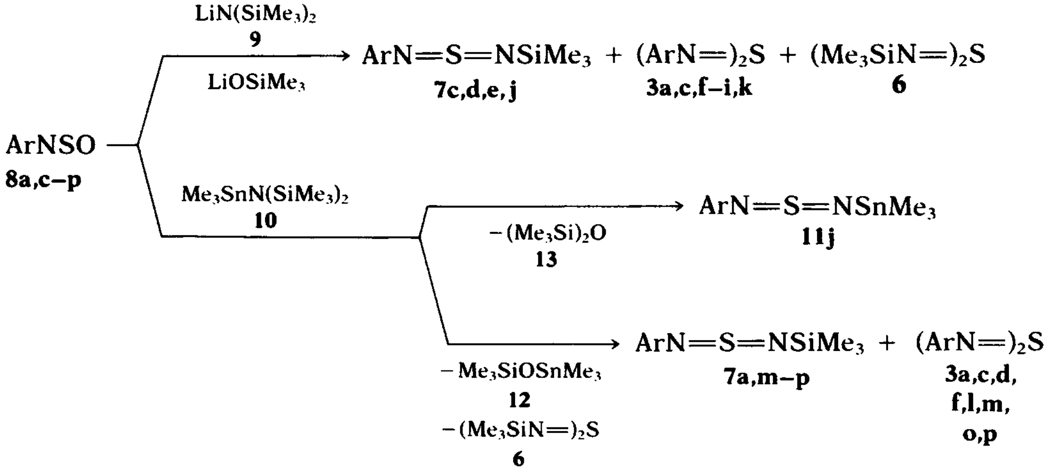
This method, however, does not afford nonsymmetric derivatives. In addition, its use for the synthesis of more extended azathienes via generation of unstable intermediates (see, e.g., Scheme 4) is inefficient [22].

The difficulties are partially eliminated by using a leaving group other than Cl in these reactions; for example, 1-phthalimidyl. The starting aza-



For a, b, c, . . . , see Scheme 2

SCHEME 1



Ar = C_6F_5 (a), 2-$O_2NC_6H_4$ (b), 4-$O_2NC_6H_4$ (c), C_6H_5 (d), 4-$CH_3C_6H_4$ (e), 4-FC_6H_4 (f), 4-JC_6H_4 (g), 4-(C_6H_5N=N)C_6H_4 (h), 2-fluorenyl (i), 2.6-$(CH_3)_2C_6H_3$ (j), 2.6-$Cl_2C_6H_3$ (k), 2.6-$F_2C_6H_3$ (l), 2,3,5,6-F_4C_6H (m), 4-$CF_3C_6F_4$ (n), 4-$CH_3C_6F_4$ (o), 4-BrC_6F_4 (p)

SCHEME 2

$$\underset{\textbf{7a,d,e,j,n}}{\mathrm{ArN{=}S{=}NSiMe_3}} \xrightarrow[-\mathrm{Me_3SiCl}]{\mathrm{SCl_2}} \underset{\textbf{5a,d,e,j,n}}{\mathrm{ArN{=}S{=}N{-}S{-}N{=}S{=}NAr}}$$

SCHEME 3

$$\underset{\textbf{7a,d,j}}{\mathrm{ArN{=}S{=}NSiMe_3}} \xrightarrow[-70^\circ\mathrm{C;\ Et_2O}]{\mathrm{SCl_2}} [\mathrm{ArN{=}S{=}N{-}SCl}] \overset{\substack{\mathrm{(Me_3SiN{=})_2S}\\ \textbf{6}}}{\underset{-70^\circ\mathrm{C;\ Et_2O}}{\text{—X}\!\longrightarrow}} \mathrm{(ArN{=}S{=}N{-}S{-}N{=})_2S}$$

SCHEME 4

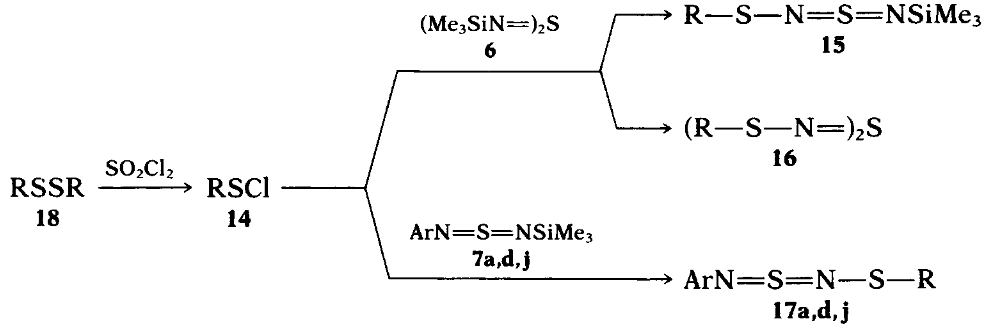
thienes containing a 1-phthalimidyl group were synthesized by using 1-phthalimidylsulfenyl chloride (**14**) as shown in Scheme 5. Compounds **17** are the analogues of the intermediates of Scheme 4, but unlike them, these compounds are quite stable.

Attempted synthesis of 1-phthalimidyl azathienes that are more extended than **15–17** by the reaction of **14** with 1,7-bis(trimethylsilyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (**19**) led to compound **16** in the reagent ratio of 2:1, and to phthalimide and **4** in the ratio 1:1. Compound **16** was also obtained in the reaction of **15** with dichloromono- and disulfanes (Scheme 6).

Substitution of the 1-phthalimidyl group in **15–17** under the action of **7** proceeds in acetonitrile in the presence of CsF. Thus, the reaction of **17d** with **7d,j** under these conditions led to the symmetric **5d** and nonsymmetric **20** azathienes respectively. The reaction of **16** and **7d** led to **5d**, and that of **17j** and **6** to **7j** (Scheme 7). The identified products of the reaction of **17d** and **19** are phthalimide and **4**. Though the fluoride ion-catalyzed desilylation of *N*-trimethylsilyl derivatives proceeds easily, it is unlikely that it takes place at the first stage of these reactions. The ^{1}H NMR spectra of reaction mixtures show that the 1-phthalimidyl group leaves azathiene molecules in the form of *N*-trimethylsilylphthalimide (**21**). The latter is subsequently desilylated; phthalimide was isolated in all cases.

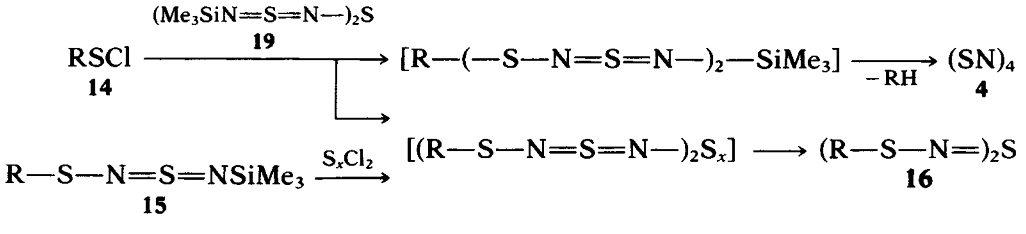
Thus, the presence of 1-phthalimidyl in the leaving group allows synthesis of nonsymmetric azathienes of type **20**. At the same time, an attempt to synthesize azathienes that were more extended than **5** and **20** failed. They are possibly formed as intermediates (see Schemes 6 and 7), but are transformed into the final products after eliminating part of the sulfur and nitrogen moieties. Apart from the indirect data, there is direct evidence of spontaneous shortening of extended sulfur–nitrogen chains. Thus, azathiene **19**, which is stable in the solid state, in alkane solutions, and even in a melt [24], is converted in acetonitrile solution at ~20°C to other compounds, of which **4** and **6** were identified [25]. Formation of the latter may be represented as shown in Scheme 8.

The data available suggest that azathienes of



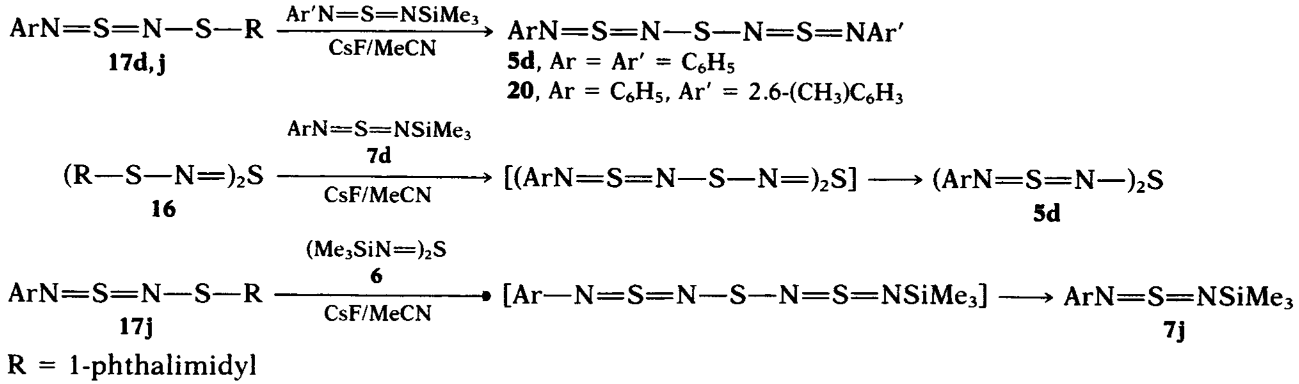
R = 1-phthalimidyl

SCHEME 5



R = 1-phthalimidyl; x = 1, 2

SCHEME 6



$$\underset{\mathbf{17d,j}}{\mathrm{ArN{=}S{=}N{-}S{-}R}} \xrightarrow[\mathrm{CsF/MeCN}]{\mathrm{Ar'N{=}S{=}NSiMe_3}} \mathrm{ArN{=}S{=}N{-}S{-}N{=}S{=}NAr'}$$

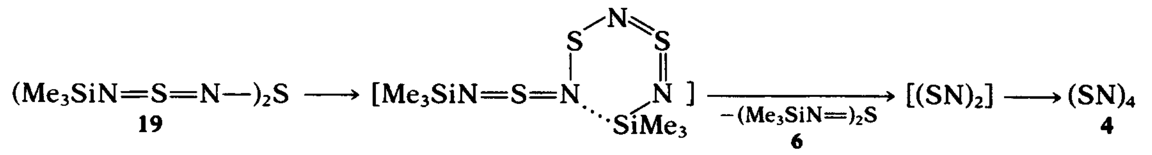
5d, Ar = Ar' = C_6H_5
20, Ar = C_6H_5, Ar' = 2.6-$(CH_3)C_6H_3$

$$\underset{\mathbf{16}}{\mathrm{(R{-}S{-}N{=})_2S}} \xrightarrow[\mathrm{CsF/MeCN}]{\underset{\mathbf{7d}}{\mathrm{ArN{=}S{=}NSiMe_3}}} \mathrm{[(ArN{=}S{=}N{-}S{-}N{=})_2S]} \longrightarrow \underset{\mathbf{5d}}{\mathrm{(ArN{=}S{=}N{-})_2S}}$$

$$\underset{\mathbf{17j}}{\mathrm{ArN{=}S{=}N{-}S{-}R}} \xrightarrow[\mathrm{CsF/MeCN}]{\underset{\mathbf{6}}{\mathrm{(Me_3SiN{=})_2S}}} \mathrm{[Ar{-}N{=}S{=}N{-}S{-}N{=}S{=}NSiMe_3]} \longrightarrow \underset{\mathbf{7j}}{\mathrm{ArN{=}S{=}NSiMe_3}}$$

R = 1-phthalimidyl

SCHEME 7



SCHEME 8

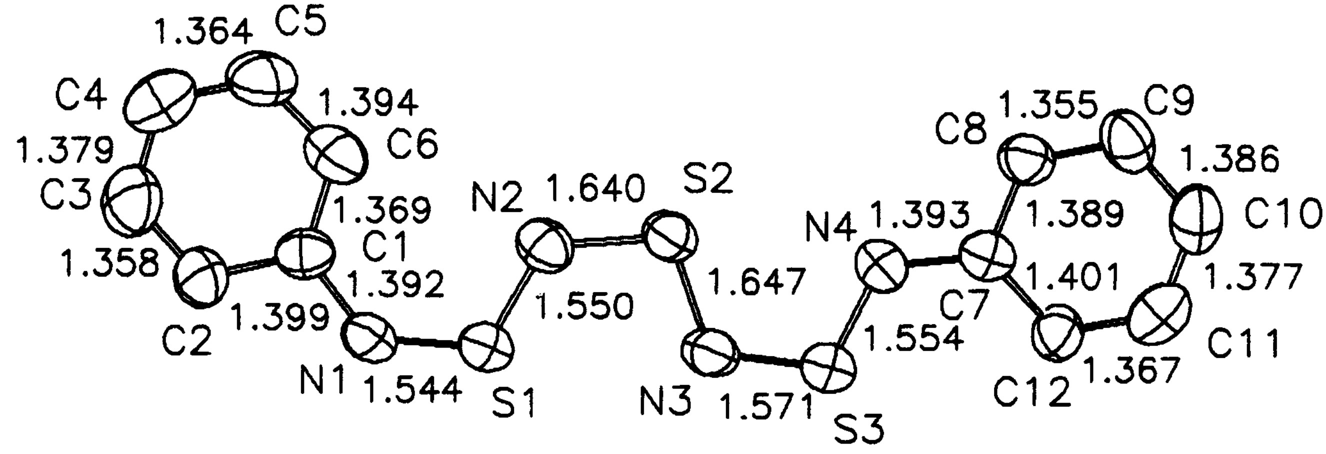
type **5**, **19**, and **20**, as well as more extended ones, are the kinetic products, whereas the shorter azathienes, such as **3**, **6**, and **7**, are the thermodynamic products. Ease of conversion of the former to the latter obviously depends on the length and structure of the azathiene chain and the organic groups in its α,ω-positions.

Crystal, Molecular, and π-Electronic Structure

According to the X-ray structure analysis data (Figures 1 and 2; Tables 1 and 2), **5d** exists in the crystal state as a planar Z,E,Z,E-isomer. The nonhydrogen atoms of the molecule lie in the same plane within ±0.14 Å; the azathiene fragment is planar within ±0.05 Å. The distances S^1–N^1, S^1–N^2, S^3–N^3, and S^3–N^4 are close to the value of 1.53–1.56 Å, which is attributed to the S=N double bond [13]. The S^2–N^2 and S^2–N^3 distances are larger, though still markedly smaller than 1.76 Å, which is the length of the ordinary S–N bond [13]. Comparison of the geometrical characteristics of acyclic azathiene molecules [10–17] shows that inequality of the SN bonds is typical. Moreover, even in $(SN)_x$, where the SN bonds are nearly identical, they are not exactly equal to each other [2]. The configuration of the azathiene chain of the **5d** molecule is similar to that of the $(SN)_x$ macromolecules [2], and significantly different from that of the E,Z,Z,E-isomers of 1,7-bis(tert-butyl)- and 1,7-bis(phenylsulfonyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraenes [16, 17], as well as *N,N'*-disulfinyldiaminosulfane [26].

The molecule of **5d** contains the secondary intramolecular bonds S· · ·N, S· · ·H, and N· · ·H. Thus, the $N^2 \cdots H^6$ distance is equal to 2.54 Å compared to 2.64 Å for the ordinary N· · ·H contact [27]. The length of C^6—H^6 in this case, at 0.65(9) Å, is very small; if it is increased to 1 Å, the $N^2 \cdots H^6$ length will be reduced to 2.32 Å. The $N^2 \cdots H^6$ interaction seems to be the cause of the increased

FIGURE 1 The molecular geometry of 1,7-bis(phenyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene, **5d** (for bond angles see Table 2). Estimated standard deviations are: SN 0.007 Å, NC 0.010 Å, CC 0.011–0.015 Å.



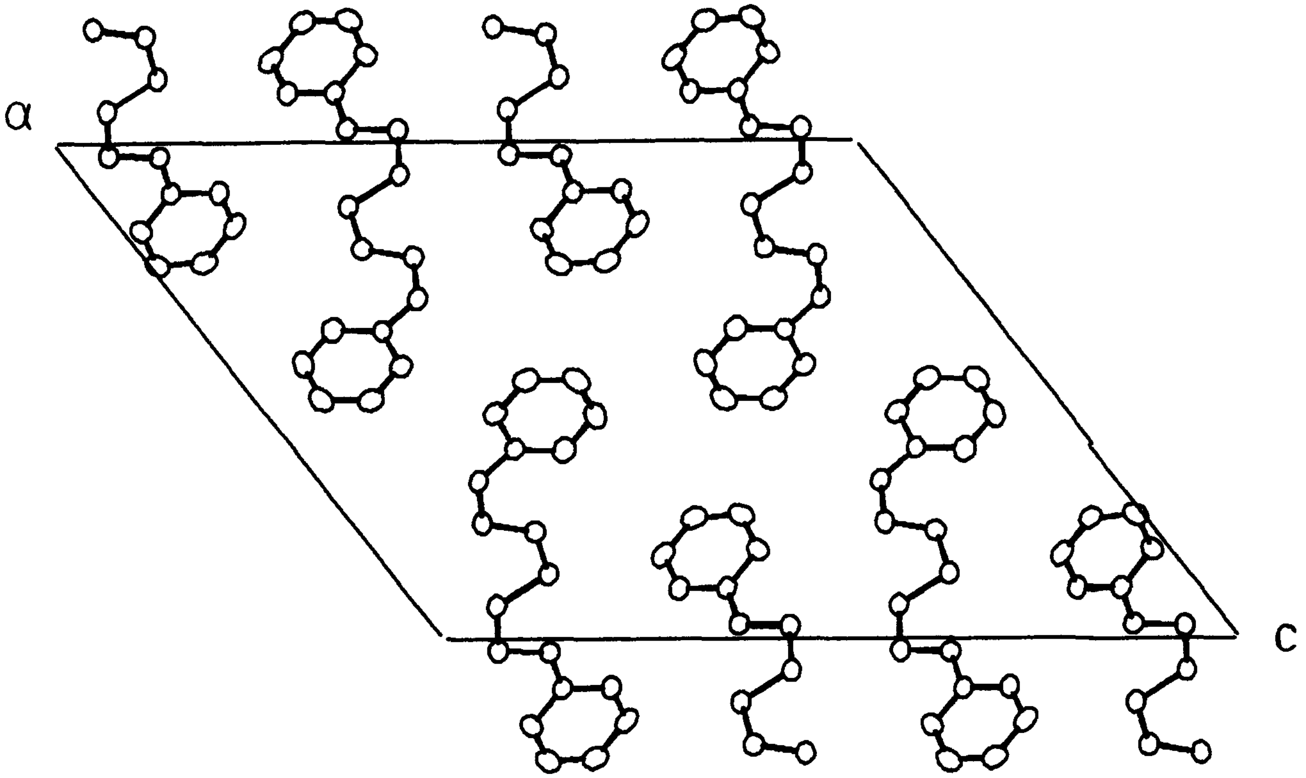


FIGURE 2 Packing of 1,7-bis(phenyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (**5d**) molecules in a crystal.

bond angles at C^1 and N^1 as compared to the angles at C^7 and N^4 (Table 2). A similar fragment in the molecules of **3e** and the 4,4′-diphenyl derivative of **3d** has an identical structure, despite the aromatic rings being turned around the C—N bonds [10, 11]. Another weak hydrogen bond C^{12}—H$^{12}\cdots$S^3 has distances 0.93(8) Å and 2.77 Å, respectively (the sum of the van der Waals radii of S and H atoms is equal to 2.94 Å [27]). The S$^1\cdots$N^3 and S$^2\cdots$N^4 distances are equal to 2.94 Å and 2.81 Å, respectively. Of intermolecular contacts, only the S$^3\cdots$S^3 one $(-x, 2-y, -z)$ is reduced to 3.60 Å. This exceeds by 0.12 Å the distance between the sulfur atoms of adjacent macromolecules in the $(SN)_x$ crystal [2].

The MNDO calculations carried out for the experimental geometry of **5d** molecule show that only 6 out of 15 of the most tightly bound π-MOs are localized on separate molecular fragments: 1a″ and 2a″ on the azathiene chain, 8a″, 9a″, 14a″, and 15a″ on the phenyl rings. The remaining 9 π-MOs, including the HOMO 11a″ and the LUMO 12a″, are delocalized throughout the whole molecule (Table 3). The simplified analysis of orbital structure in terms of the fragmentary approach enables one to estimate the efficiency of intramolecular interactions leading to formation of π-MOs over the whole molecule of **5d**. Thus, the energy difference between MOs 6a″ and 10a″, corresponding to the bonding

TABLE 1 Atomic Coordinates ($\times 10^4$) of **5d** Molecule[a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S^1	2321(2)	1840(6)	1623(1)	S^2	1297(2)	5521(5)	1939(1)
S^3	−0247(2)	7988(6)	0566(1)	N^1	3166(5)	−0395(17)	1986(4)
N^2	2152(5)	3132(15)	2188(4)	N^3	0658(5)	5859(16)	0990(4)
N^4	−0285(5)	9451(15)	1188(4)	C^1	3806(6)	−1529(19)	2735(5)
C^2	4524(7)	−3398(22)	2847(6)	C^3	5195(8)	−4610(30)	3558(7)
C^4	5184(9)	−4075(28)	4174(7)	C^5	4478(9)	−2259(25)	4058(6)
C^6	3781(10)	−0957(29)	3338(7)	C^7	−1016(6)	11446(17)	0986(4)
C^8	−0996(7)	12543(19)	1588(5)	C^9	−1673(7)	14487(22)	1459(6)
C^{10}	−2413(8)	15458(23)	0711(7)	C^{11}	−2472(7)	14328(25)	0100(6)
C^{12}	−1774(7)	12424(20)	0232(5)				
H^6	3450(72)	−0118(227)	3299(61)	H^{12}	−1860(62)	11672(194)	−0133(49)

[a] Estimated standard deviations are in parentheses.

TABLE 2 Bond Angles (°) in a Molecule of **5d**[a]

$N^2S^1N^1$	115.3(4)	$N^3S^2N^2$	104.2(3)	$N^4S^3N^3$	108.6(4)
$C^1N^1S^1$	131.8(6)	$S^2N^2S^1$	124.4(4)	$S^3N^3S^2$	116.6(4)
$C^7N^4S^3$	121.9(5)	$C^2C^1N^1$	114.2(7)	$C^6C^1N^1$	125.9(9)
$C^6C^1C^2$	119.9(9)	$C^3C^2C^1$	119.4(10)	$C^4C^3C^2$	121.8(12)
$C^5C^4C^3$	118.4(11)	$C^6C^5C^4$	121.4(11)	$C^5C^6C^1$	119.1(12)
$C^8C^7N^4$	116.9(7)	$C^{12}C^7N^4$	126.1(7)	$C^{12}C^7C^8$	117.1(8)
$C^9C^8C^7$	121.9(9)	$C^{10}C^9C^8$	120.3(10)	$C^{11}C^{10}C^9$	118.9(10)
$C^{12}C^{11}C^{10}$	120.6(10)	$C^{11}C^{12}C^7$	121.0(9)		

[a] Estimated standard deviations are in parentheses.

and antibonding combinations of the same set of fragment orbitals, is 2.29 eV; in another similar case, the energy difference between MOs 3a″ and 5a″ is 1.52 eV (Table 3).

Thus, the molecular geometry and π-electronic structure of **5d** show that creation of a molecular wire for MED on the basis of extended azathienes is really possible. In the future, we are planning the syntheses of compounds **5** containing stable radicals as ring substituents, and experimental ESR studies on their intramolecular electron conductivity.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Varian A56/60A spectrometer (60 and 56.4 MHz respectively, internal standards HMDs and C_6F_6). The ^{13}C, ^{14}N, ^{15}N, and ^{119}Sn NMR spectra were recorded on a Bruker CXP-300 spectrometer (75.46, 21.26, 30.42, and 111.83 MHz respectively; the standards were internal TMS, external $MeNO_2$, and Me_4Sn; the nitrogen NMR chemical shifts are given relative to NH_3). The ^{29}Si NMR spectra were recorded on Bruker AM-400 and CXP-300 spectrometers (79.50 and 59.62 MHz, respectively, internal standard TMS). Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT MS-8200 instrument. The UV-visible spectra were collected on Beckman DU-8 and Specord M40 spectrometers, and the IR spectra on an IR-75 instrument.

Thermogravimetric measurements were carried out on a MOM derivatograph, He, 10°C/min. The GLC analysis was fulfilled on an LKM-72 chromatograph (50–270°C), 4000 × 4 mm, SKTFW-803 on a Chromosorb W, 15:100, He, 60 mL/min.

The X-ray structure analysis was carried out on a Syntex $P2_1$ diffractometer using the MoK_α radiation with graphite monochromator. The crystals of **5d** are monoclinic: a = 17.183(6), b = 4.623(1), c = 21.827(8) Å, β = 128.11(2)°, space group $P2_1/c$, Z = 4, D_c = 1.49 g/cm^3. The intensities of 1811 independent reflections were measured by the $2\theta/\theta$ scanning method in the $2\theta < 50°$ range; 1435 reflections with $I > 2\sigma$ were used in calculations without correction on absorption (μ = 5.2 cm^{-1}). The structure was solved by the heavy atom method using the SHELXS-86 program. The H atom positions were

TABLE 3 MNDO Data on the π-Electronic Structure of a Molecule of **5d**

π-MOs	*$-\varepsilon$, eV*[a]	*π-MOS Composition*[b]
1a″	15.25	$1\pi + \pi_S + 1\pi'$
2a″	14.75	$1\pi - 1\pi'$
3a″	13.38	$a_{2u} + 2\pi + \pi_S + 2\pi' + a'_{2u}$
4a″	12.86	$a_{2u} + 2\pi - 2\pi' + a'_{2u}$
5a″	11.86	$a_{2u} - 2\pi + \pi_S + 2\pi' - a'_{2u}$
6a″	11.03	$e_{1g}S + 2\pi - 2\pi' + e_{1g}S'$
7a″	9.80	$e_{1g}A + 2\pi - \pi_S - 2\pi' + e_{1g}S'$
8a″	9.72	$e_{1g}A$
9a″	9.41	$e_{1g}A'$
10a″	8.74	$e_{1g}S - 2\pi - 2\pi' - e_{1g}S'$
11a″ (HOMO)	7.73	$e_{1g}S - 2\pi - \pi_S - 2\pi' - e_{1g}S'$
12a″ (LUMO)	2.27	$e_{2u}S + 3\pi - \pi_S + 3\pi' + e_{2u}S'$
13a″	1.50	$e_{2u}S + 3\pi - \pi_S - 3\pi' + e_{2u}S'$
14a″	0.12	$e_{2u}A$
15a″	−0.45	$e_{2u}A'$

[a] The one-electron energy of MO with an opposite sign.

[b] The 1π, 2π, and 3π are the quasiallyl π-orbitals of the —N=S=N— fragment (the bonding, nonbonding, and antibonding ones, respectively). a_{2u}, $e_{1g}S$, $e_{1g}A$, $e_{2u}S$, and e_{2u} A are the group π-orbitals of the phenyl rings correlating with π-MOs of benzene $1a_{2u}$, $1e_{1g}$, and $1e_{2u}$ respectively. π_S is the 3p-AO of the sulfur atom S^2.

calculated geometrically. Final structure refinement was carried out by the least squares method in the block-diagonal anisotropic-isotropic (for H atoms) approximation to $R = 0.0774$, $R_w = 0.0791$, where $w^{-1} = \sigma^2 + 0.000436\ F^2$.

The MNDO calculations were performed using the AMPAC program (the ES version [28]).

Compounds **3a–e**, **4**, **5a**, **6**, **7d**, **12**, **13**, **21** were identified on the basis of the data reported in Refs.

TABLE 4 The Compounds Synthesized

Compound	mp (°C), bp (°C/mm)	Yield %	Formula	Found (%) (calculated)				
				C	H	N	S	F/Cl
3f	94–95	56	$C_{12}H_8F_2N_2S$	57.8	3.1	11.2	12.7	14.9
				(57.6	3.2	11.2	12.8	15.2)
3g	117–118	80	$C_{12}H_8I_2N_2S$	30.7	1.4	5.9	7.1	
				(30.9	1.7	6.0	6.9)	
3i	176–177	64	$C_{26}H_{18}N_2S$	79.8	4.4	7.2	8.4	
				(80.0	4.6	7.2	8.2)	
3k	137–138	74	$C_{12}H_6Cl_4N_2S$	40.7	1.5	7.9	8.5	40.1
				(40.9	1.7	8.0	9.1	40.3)
3l	108–109	50	$C_{12}H_6F_4N_2S$	50.0	2.2	9.6	11.2	26.9
				(50.4	2.1	9.8	11.2	26.6)
3p	80–82	19	$C_{12}Br_2F_4N_2S^a$					
5d	84–85	70	$C_{12}H_{10}N_4S_3{}^b$	46.9	3.0	18.4	31.0	
				(47.1	3.3	18.3	31.4)	
5e	106–107	86	$C_{14}H_{14}N_4S_3$	50.1	3.9	16.6	28.6	
				(50.3	4.2	16.8	28.7)	
5j	87–88	70	$C_{16}H_{18}N_4S_3$	52.7	5.0	15.4	26.4	
				(53.0	5.0	15.5	26.5)	
5n	90–91	57	$C_{14}F_{14}N_4S_3$	28.8		9.6	16.3	45.1
				(28.7		9.6	16.4	45.4)
7a	78–79/2	65	$C_9H_9F_5N_2SSi$	36.2	3.0	9.0	10.6	31.7
				(36.0	3.0	9.3	10.7	31.7)
7c	145/1,	26	$C_9H_{13}N_3O_2SSi^a$	42.1	5.0	16.0	12.5	
	51–53			(42.4	5.1	16.5	12.5)	
7e	83–84/0.1	65	$C_{10}H_{16}N_2SSi$	54.2	6.6	12.5	14.4	
				(54.1	6.3	12.6	14.5)	
7j	80–81/1	63	$C_{11}H_{18}N_2SSi^a$	55.2	7.6	11.7	13.6	
				(55.5	7.6	11.8	13.5)	
7m	80–81/2	50	$C_9H_{10}F_4N_2SSi$	38.2	3.4	9.7	11.1	26.9
				(38.3	3.6	9.9	11.4	27.0)
7n	83–84/2	85	$C_{10}H_9F_7N_4SSi$	34.5	3.0	7.7	8.8	38.1
				(34.3	2.6	8.0	9.1	38.0)
7o	85–86/2	40	$C_{10}H_{12}F_4N_2SSi$	40.7	4.0	9.0	10.5	25.4
				(40.5	4.1	9.5	10.8	25.7)
7p	98/2	58	$C_9H_9BrF_4N_2SSi^a$					
11j	99–100/2	25	$C_{11}H_{18}N_2SSn$	40.2	5.6	8.2	9.6	
				(40.2	5.5	8.5	9.7)	
14	138–139	55	$C_8H_4ClNO_2S$	45.6	2.0	6.6	14.5	16.8
				(45.0	1.9	6.6	15.0	16.6)
15	76–77	65	$C_{11}H_{13}N_3O_2S_2Si$	42.4	4.1	13.5	20.4	
				(42.4	4.2	13.5	20.6)	
16	196–197	80	$C_{16}H_8O_4S_3$	46.3	1.9	13.8	23.4	
	(decomp.)			(46.2	1.9	13.5	23.1)	
17a	181–183	60	$C_{14}H_4F_5N_3O_2S_2$	41.8	1.0	10.4	16.0	23.5
				(41.5	1.0	10.4	15.8	23.5)
17d	177–179	80	$C_{14}H_9N_3O_2S_2$	53.6	2.9	13.3	20.2	
				(53.3	2.9	13.3	20.3)	
17j	141–142	75	$C_{16}H_{13}N_3O_2S_2$	56.2	3.8	12.0	18.2	
				(56.0	3.8	12.2	18.7)	
20	58–60	11	$C_{14}H_{11}N_4S_3{}^a$	50.3	4.0	16.8	29.0	
				(50.3	4.2	16.8	28.7)	

[a] M^+, m/z, measured (calculated): **3p**, 513.8061 (513.8022, ^{79}Br); **7c**, 255.0451 (255.0498); **7j**, 238.0955 (238.0960); **7p**, 359.9379 (359.9376, ^{79}Br); **20**, 334.0384 (334.0381).

[b] M, ebullioscopy in $CHCl_3$, measured (calculated): 303 (306).

TABLE 5 NMR and UV-Visible Data

Compound	NMR[a]			UV-visible λ_{max}, nm, (lg ε)[b]
	δ^{1}H	δ^{19}F	δ Other Nuclei	
1	0.18		1.57 (^{13}C), 13.1 (^{15}N), 9.3 (^{29}Si)	<200
3f		48.4		426(3.94)
3g				442(4.18)
3i				486(4.39)
3k	6.91[c]			407(3.15)
3l	7.22–6.41	45.8		416(3.34)
3p		29.6, 22.7		411(3.86)
5a		17.3, 3.9, −0.2		526(4.35)
5d	7.26[c]		121.3, 129.1, 126.6, 145.0 (^{13}C)	522(4.31)
5e	7.16[c], 2.34, 0.29			530(4.34)
5j	6.82, 2.03			451(4.02)
5n		106.3, 21.3, 18.4		529(4.35)
6	0.21		323 (^{14}N), 0.5 (^{29}Si)	273(4.07)
7a	0.19	18.8, 1.7, −1.1	317, 268 (^{14}N), 5.8 (^{29}Si)	325(3.61)
7c	8.41–7.70, 0.42		369, 320, 294 (^{14}N), 6.7 (^{29}Si)	339(4.22)
7d	7.46[c], 0.16		124.5, 128.8, 126.9, 145.4, 1.1 (^{13}C), 3.3 (^{29}Si)	332(4.03)
7e	7.03[c], 1.99, 0.06			335(4.09)
7j	6.83[c], 2.03, −0.18		314, 290 (^{14}N), 1.0 (^{29}Si)	382(2.86)
7m	6.77, 0.13	22.7, 17.7		326(3.54)
7n	0.19	107.2, 20.9, 19.7	328, 266 (^{14}N), 7.4 (^{29}Si)	318(3.67)
7o	2.15, 0.13	17.8, 16.9		332(3.62)
7p	0.18	27.5, 19.3		323(3.63)
10	0.25[d], 0.06		24 (^{14}N), 1.6 (^{29}Si), 53.3 (^{119}Sn)[e]	
11j	6.87, 2.05, 0.09[f]			325(3.04)
14	7.95[c]			304(3.31)
15	7.85[c], 0.19		5.4 (^{29}Si)	344(4.20)
16	7.87[c]			400(3.76)
17a	7.90[c]	16.4, 2.5, −0.6		415(4.24)
17d	7.86[c], 7.21[c]			421(4.02)
17j	7.78[c], 7.00, 2.25			417(3.45)
19	0.29		5.6 (^{29}Si)	488(3.52)
20	7.32–6.80, 2.13			507(419)
21	7.69, 0.43	17.8, 13.0 (^{29}Si)[g]		

[a] Solvents: ^{1}H, **1, 3k, 6, 19, 20**: $CDCl_3$; **3l**: CH_3CN; **5d, 14–17a,d,j**: CH_2Cl_2; **5j, 7c, 11j, 21**: CCl_4; **7a,d,e,j,m–p, 10**: neat liquids. ^{19}F, **3f,p**: CCl_4; **3l**: CH_3CN; **5a,n**: $CHCl_3$; **17a**: CH_2Cl_2; **7a,m–p**: neat liquids. ^{13}C, $CHCl_3$. ^{14}N, ^{15}N, **1**: CCl_4; **6, 7a,c,n**: $CHCl_3$; **7j, 10**: $CDCL_3$. ^{29}Si, **1, 6, 7a,c,d,n, 10, 19**: $CHCl_3$; **7j, 15, 21**: $CDCl_3$. ^{119}Sn, $CHCl_3$.

[b] Solvents: **1, 3f,k,l,p, 5j, 7a,c,e,j,m,n,p, 11j, 15, 20**: heptane; the remaining ones: $CHCl_3$.

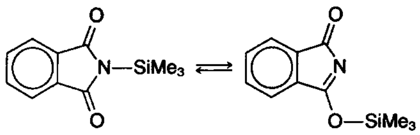
[c] Center of the multiplet.

[d] J (^{1}H—^{119}Sn) 56 Hz, J (^{1}H—^{117}Sn) 54.5 Hz.

[e] J (^{119}Sn—^{1}H) 54 ± 3 Hz.

[f] J (^{1}H—^{119}Sn) 59.5 Hz, J (^{1}H—^{117}Sn) 57.5 Hz.

[g] Equilibrium



[21, 29–37]. The data for compounds synthesized for the first time are listed in Tables 4 and 5.

The starting compounds were synthesized by the procedures: **1** [38], **2a** [31], **2b,c** [39], **6** [34], **8** [40], **18** [41], **19** [42]. Compound **10** in an 80% yield was obtained by analogy with Ref. [43] by heating a 1:1 mixture of **9** and Me_2SnCl for 3 h at 120°C.

The syntheses described below were performed in absolute solvents and, except for **14**, in an argon atmosphere. Cesium fluoride was calcined immediately before use. The reagents were added dropwise, and the solvents were distilled off from the reaction mixtures at reduced pressure.

Reaction of N,N,N′,N′*-Tetrakis(trimethylsilyl)-diaminosulfane* (**1**) *with* S,S*-Dichloro-*N*-aryliminosulfuranes* (**2a–c**)

a) A solution of 0.01 mol of **2** in 15 mL of Et_2O was added to a stirred solution of 1.76 g (0.005 mol) of

1 in 25 mL of Et_2O at 20°C. After 2 h the solvent was distilled off.

2a: The solid residue was sublimed in vacuum at 1 mm; at 40–45°C, 1,3-bis(pentafluorophenyl)-1,3-diaza-2-thiaallene (**3a**, purified by resublimation, 1.58 g); at 80–85°C, a mixture of cyclotetra(azathiene) (**4**) and 1,7-bis(pentafluorophenyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (**5a**). Compound **5a** was extracted with CCl_4, the solvent was distilled off, and the residue resublimed. Purple crystals, mp 100°C (102°C [21]), 0.17 g (7%). Compound **4**, which is insoluble in CCl_4, was purified by resublimation, 0.36 g.

2b: The residue was dissolved in acetone and the undissolved part was sublimed in vacuum: **4**, 0.35 g. Acetone was distilled off, and the residue was recrystallized from the benzene–hexane mixture. 1,3-Bis(2-nitrophenyl)-1,3-diaza-2-thiaallene (**3b**, 1.18 g).

2c: The residue was recrystallized from toluene. 1,3-Bis(4-nitrophenyl)-1,3-diaza-2-thiaallene (**3c**, 1.21 g). The mother liquor was concentrated and chromatographed on a silica gel column (benzene): **4**, 0.33 g.

b) Under the same conditions as above, 0.01 mol of **1** was reacted with 0.01 mole of **2**. After the solvent had been distilled off, the residue was sublimed in vacuum (**3a**, 0.049 mol) or recrystallized (**3b**, benzene–hexane, 0.049 mol; **3c**, chloroform, 0.048 mol).

Reaction of Lithium N,N-*Bis(trimethylsilyl)amide* (**9**) *with* N-*Sulfinylarylamines* (**8**)

1-Aryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes (**7c, d,e,j**). a) A solution of 0.06 mol of **8d,e,j** in 15 mL of Et_2O was added to a stirred suspension of 10.0 g (0.06 mol) of **9** in 50 mL of Et_2O at −15°C. After 2 h the temperature was raised to 20°C, and a solution of 6.6 g (0.06 mol) of trimethylchlorosilane in 10 mL of Et_2O was added. After 2 h the residue was filtered off, the solvent was distilled off, and the residue was distilled in vacuum: **7d** (70%), **7e,j**, orange oils.

b) A solution of 5.5 g (0.03 mol) of **8c** in 25 mL of Et_2O was added to a stirred suspension of 5.0 g (0.03 mol) of **9** in 100 mL of Et_2O at −70°C. The temperature was raised to 0°C during 4 h, then a solution of 3.3 g (0.03 mol) of trimethylchlorosilane in 20 mL of Et_2O was added. The temperature was raised to 20°C during 2 h, the solution was filtered, the solvent was distilled off, and the residue was distilled in vacuum: **7c**, bright yellow crystals.

c) 1,3-Bis(pentafluorophenyl)-, 1,3-bis(4-fluorophenyl)-, 1,3-bis(4-iodophenyl)-, 1,3-bis(2,6-dichlorophenyl)-1,3-diaza-2-thiaallenes (**3a,f,g,k**) were obtained by the reaction of **9** with **8a,f,g,k** under the conditions described in paragraph "a". After the solvent had been distilled off, the residue was recrystallized from hexane (**3a**, 40%; **3f**, 56%) or benzene (**3g**, 80%; **3k**, 74%).

1,3-Bis[4-(phenylazo)phenyl]- and 1,3-bis(2-fluorenyl)-1,3-diaza-2-thiaallenes (**3h,i**) were synthesized in a similar way, except for the fact that trimethylchlorosilane was not added. The precipitate was filtered off and recrystallized from toluene: **3h**, (72%), **3i**.

*Reaction of 1,1,1-Trimethyl-*N,N-*bis(trimethylsilyl)stannaneamine* (**10**) *with* N-*Sulfinylarylamines* (**8**)

1-Polyfluoraryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes (**7a,m–p**). A mixture of 0.015 mol of **10**, 30 mL of acetonitrile, and 0.015 mol of **8** was boiled for 15 min in the case of **8a,c,m–p**, for 2 h in the case of **8d,f,l**, and for 8 h in the case of **8j**. Acetonitrile, hexamethylsilstanoxane (**12**), 1,3-bis(trimethylsilyl)-1.3-diaza-2-thiaallene (**6**), or hexamethyldisiloxane (**13**) were distilled off, and the residue was distilled in vacuum: **7a,m–p, 11j**, orange-red oils. The solid stillage residue was recrystallized from hexane: **3a** (10%), **3c** (75%), **3m** (10%), **3o** (30%), **3f,l,p**, orange or red crystals.

1-Phthalimidylsulfenyl Chloride (**14**). Di(1-phthalimidyl)disulfane (**18**) was boiled with excess sulfuryl chloride until a true solution had formed, then the solvent was distilled off, and the residue was recrystallized from CCl_4: **14**, pale yellow crystals.

1-Trimethylsilyl-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadiene (**15**) *and 1,5-Bis(1-phthalimidyl)-2,4-diaza-1,3,5-trithia-2,3-pentadiene* (**16**). A solution of 1.28 g (0.006 mol) of 1-phthalimidylsulfenyl chloride (**14**) in 10 mL of CH_2Cl_2 was added at 20°C to a stirred solution of a) 1.24 g (0.006 mol) or b) 0.62 g (0.003 mol) of 1,3-bis(trimethylsilyl)-1,3-diaza-2-thiaallene (**6**) in 5 mL of CH_2Cl_2. After a) 5 h or b) 24 h, the solvent was distilled off and the residue was recrystallized: a) From hexane, **15**, light-creme glittering flakes; b) From acetonitrile, **16**, orange crystals.

1-Aryl-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadienes (**17a,d,j**). A solution of 0.02 mol of 1-aryl-3-trimethylsilyl-1,3-diaza-2-thiaallene (**7**) in 10 mL of CH_2Cl_2 was added at 20°C to a stirred solution of 4.27 g (0.02 mol) of 1-phthalimidylsulfenyl chloride (**14**) in 30 mL of CH_2Cl_2. After 10 h, the solvent was distilled off and the residue was recrystallized from a benzene–heptane mixture: **17a,d,j**, orange crystals.

Reaction of 1-Phthalimidylsulfenyl Chloride (**14**) *with 1,7-Bis(trimethylsilyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene* (**19**)

A solution of 0.43 g (0.002 mol) of **14** in 10 mL of THF was added at −50°C to a stirred solution of a) 0.60 g (0.002 mol) or b) 0.30 g (0.001 mol) of **19** in 20 mL of THF. After 2 h, the temperature was raised to 20°C, and the solvent was distilled off. The residue was: a) Recrystallized from benzene. Phthalimide, 0.19 g (65%). The benzene solution was evaporated, and the residue was sublimed in vacuum. Cyclotetra(azathiene) (**4**), 0.15 g (58%). b) Recrystallized from acetonitrile. 1,5-Bis(1-phthalimidyl)-2,4-diaza-1,3,5-trithia-2,3-pentadiene (**16**), 0.30 g (70%).

Reaction of 1-Trimethylsilyl-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadiene (**15**) *with Dichloromono- and disulfanes*

A solution of 0.002 mol of S_2Cl_2 or freshly prepared SCl_2 in 5 mL of Et_2O was added at −70°C to a stirred solution of 1.24 g (0.004 mol) of **15** in 20 mL of Et_2O. After 1 h the temperature was raised to 20°C, the solvent was distilled off, and the residue was recrystallized from acetonitrile: 1,5-Bis(1-phthalimidyl)-2,4-diaza-1,3,5-trithia-2,3-pentadiene (**16**), 0.62 g (75%).

1,7-Bis(aryl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraenes (**5**) *and 1-(2,6-Dimethylphenyl)-7-phenyl-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene* (**20**). a) A solution of 0.52 g (0.005 mol) of freshly prepared SCl_2 in 5 mL of Et_2O was added at −50°C to a stirred solution of 0.01 mol of 1-aryl-3-trimethylsilyl-1,3-diaza-2-thiaallene (**7**) in 15 mL of Et_2O. After 1 h the temperature was raised to 20°C, the solvent was distilled off, and the residue was recrystallized from hexane: **5a** (60%, mp 108–109°C (102°C [21])); **5d,e,n**, dark green crystals with golden glitter; **5j**, dark crystals.

b) To a stirred mixture of 0.95 g (0.003 mol) of 1-phenyl-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadiene (**17d**) and 0.63 g (0.003 mol) of 1-phenyl-3-trimethylsilyl-1,3-diaza-2-thiaallene (**7d**) in 50 mL of acetonitrile at 20°C was added 0.46 g (0.003 mol) of CsF. After 3 h the reaction mixture was filtered, the solvent was distilled off, and the residue was recrystallized from hexane: **5d**, 0.28 g (30%).

c) A mixture of 0.71 g (0.003 mol) of 1-(2,6-dimethylphenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallene (**7j**) and 0.46 g (0.003 mol) of CsF in 100 mL of acetonitrile was stirred for 5 h at 20°C, then 0.95 g (0.003 mol) of 1-phenyl-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadiene (**17d**) was added. After 10 min the precipitate that had formed was filtered off, the solvent was distilled off, and the residue was recrystallized from pentane: **20**, green glittering crystals.

Reaction of 1,5-Bis(1-phthalimidyl)-2,4-diaza-1,3,5-trithia-2,3-pentadiene (**16**) *with 1-Phenyl-3-trimethylsilyl-1,3-diaza-2-thiaallene* (**7d**)

A solution of 0.21 g (0.001 mol) of **7d** in 10 mL of acetonitrile was added to a stirred suspension of 0.21 g (0.0005 mol) of **16** and 0.15 g (0.001 mol) of CsF in 40 mL of acetonitrile at 20°C. After 2 h the mixture was filtered, the solvent was distilled off, and the residue was recrystallized from hexane: 1,7-bis(phenyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (**5d**), 0.09 g (45%).

Reaction of 1-Phenyl-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadiene (**17d**) *with 1,7-Bis(trimethylsilyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene* (**19**)

To a stirred mixture of 0.30 g (0.001 mol) of **19** and 0.31 g (0.002 mol) of CsF in 50 mL of acetonitrile was added at 20°C during 15 min 0.63 g (0.002 mol) of **17d**. After 3 h the mixture was filtered, the solvent was distilled off, and the residue was recrystallized from $CHCl_3$ and sublimed in vacuum: Phthalimide, 0.21 g (70%). Chloroform was distilled off, and the residue was sublimed in vacuum: Cyclotetra(azathiene) (**4**), 0.11 g.

Reaction of 1-(2,6-Dimethylphenyl)-4-(1-phthalimidyl)-1,3-diaza-2,4-dithia-1,2-butadiene (**17j**) *with 1,3-Bis(trimethylsilyl)-1,3-diaza-2-thiaallene* (**6**)

To a boiling solution of 1.03 g (0.003 mol) of **17j** and 0.62 g (0.003 mol) of **6** in 10 mL of acetonitrile was added 0.46 g (0.003 mol) of CsF. After 2 h the solvent was distilled off, and the residue was extracted with 20 mL of hexane. The undissolved compound was recrystallized from $CHCl_3$: Phthalimide, 0.26 g (60%). The hexane solution was evaporated, and the residue was distilled in vacuum at 80°C/1 mm. 1-(2,6-Dimethylphenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallene (**7j**), 0.43 g (60%).

N-Trimethylsilylphthalimide (**21**). .A mixture of 10.0 g of potassium phthalimide, 50 mL of benzene, and 16 mL of trimethylchlorosilane was boiled for 5 h and filtered. The solvent was then distilled off and the residue was recrystallized from hexane: **21**, 8.88 g (75%).

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[20] Compound **5a** reported earlier was synthesized by a nonrational method in a 0.6% yield and its structure was not established [21]. It should be noted that for use as a molecular wire, connecting the MED elements with different functions, nonsymmetric azathienes are mostly required.

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[22] At Ar = Ph, the intermediate of Scheme 4 may cyclize to 1,3,2,4-benzodithiadiazine [23]. The protection of ortho-positions (Ar = C_6F_5, 2,6-$(CH_3)_2C_6H_3$) also fails to lead to the desired result.

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[24] As shown by the thermogravimetric data, on heating in helium, compound **19** melts at 70°C and exothermally decomposes only at 175°C.

[25] Immediately after preparation of the acetonitrile-d_3 solution of **19** saturated at ~20°C, its ^{29}Si NMR spectrum presents a singlet with δ 4.1 ppm. After 10 days its spectrum consists of singlets with δ 6.2, 6.0, and 1.0 (**6**) ppm with the intensity ratio 3.5:1.3:1.0. The GLC confirms the presence of three main products in solution with the ratio 3.6:1.8:1.0 (**6**). Compound **6** was identified by comparison of the ^{29}Si NMR spectra and chromatograms with those of the authentic sample. A crystalline precipitates of **4** was isolated from the solution (70%).

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