2,3,8,9-Dibenzo-5,6-(substituted)benzo-1,4-dithio-7-azacyclonona-2,5,8-trienes. Synthesis and Mechanistic Study

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5-(2-Acetamidoaryl)thianthreniumyl perchlorates reacted with potassium hydroxide in methanol at reflux giving 2,3,8,9-dibenzo-5,6-(substituted)benzo-1,4-dithio-7-azacyclonona-2,5,8-trienes **4** in 43 to 75% yields, whereas the reactions of the same compounds with sodium hydride in the absence or in the presence of dimethyl sulfate in refluxing tetrahydrofuran gave *N*-acetylated and *N*-methylated **4** in 68 to 96% and 27 to 56% yields, respectively. The mechanism of the formation of the products might be explained by a nucleophilic attack of amide ions **10**, **12**, and **14** at the *ipso*-position of the thianthrene ring. A sulfuranyl radical mechanism might be involved in these reactions.

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Previously we reported a simple method for the synthesis of 2-arylthio-2'-arylthiodiphenyl sulfides **1** which involved the reactions of 5-arylthianthreniumyl perchlorates **2** with arylthiolates in tetrahydrofuran at reflux [1]. In the course of study to explore the potential utilities of **2** for the synthesis of the sulfur containing compounds, we were aware that only one example for the thiacrown compounds with 2,2'-dithiodiphenyl sulfide moiety had been reported [2]. One of the reasons for receiving lesser attention might be due to the difficulty in synthesis of polythioethers consisting of only *ortho* thioether linkages. It was our original intention to synthesize trithiadiazaoxa cyclic compounds **3**, by employing our methodology involving the reaction of 5-(2-aminoaryl)thianthreniumyl perchlorates **2** ($R^1 = NH_2$) with 2-aminophenylthiolate, followed by a series of the conventional procedures (Scheme 1). Since compounds **2** ($R^1 = NH_2$) could not be directly synthesized by the reaction of thianthrene cation radical perchlorate with aromatic amines [3], 5-(2-acetamido-4,5-dimethylphenyl)thianthreniumyl perchlorate (**2b**) was synthesized by the reaction with 3,4-dimethylacetanilide according to the literature procedures [4] and then hydrolysis of the acetamido group of **2b** with potassium hydroxide in methanol at reflux was carried out to obtain 5-(2-amino-4,5-dimethylphenyl)thianthreniumyl perchlorate (**2**) ($R^1 = NH_2$, $R^2 = H$, $R^3 = R^4 = CH_3$). Surprisingly, 2,3,8,9-dibenzo-5,6-(3,4-dimethyl)benzo-1,4-dithia-7-azacyclonona-2,5,8-triene (**4b**) was obtained as a major product. The formation of **4b** was of interest in the light of the first example for dithiaaza cyclic compounds which might not be readily available by the conventional synthetic methods. Therefore, the cyclization reactions were studied in detail. The results are described herein.

Results.

Various acetamido compounds **2** ($R^1 = NHCOCH_3$) prepared [4] including their physical and analytical data, and reaction times are summarized in Table 1 and their ir and

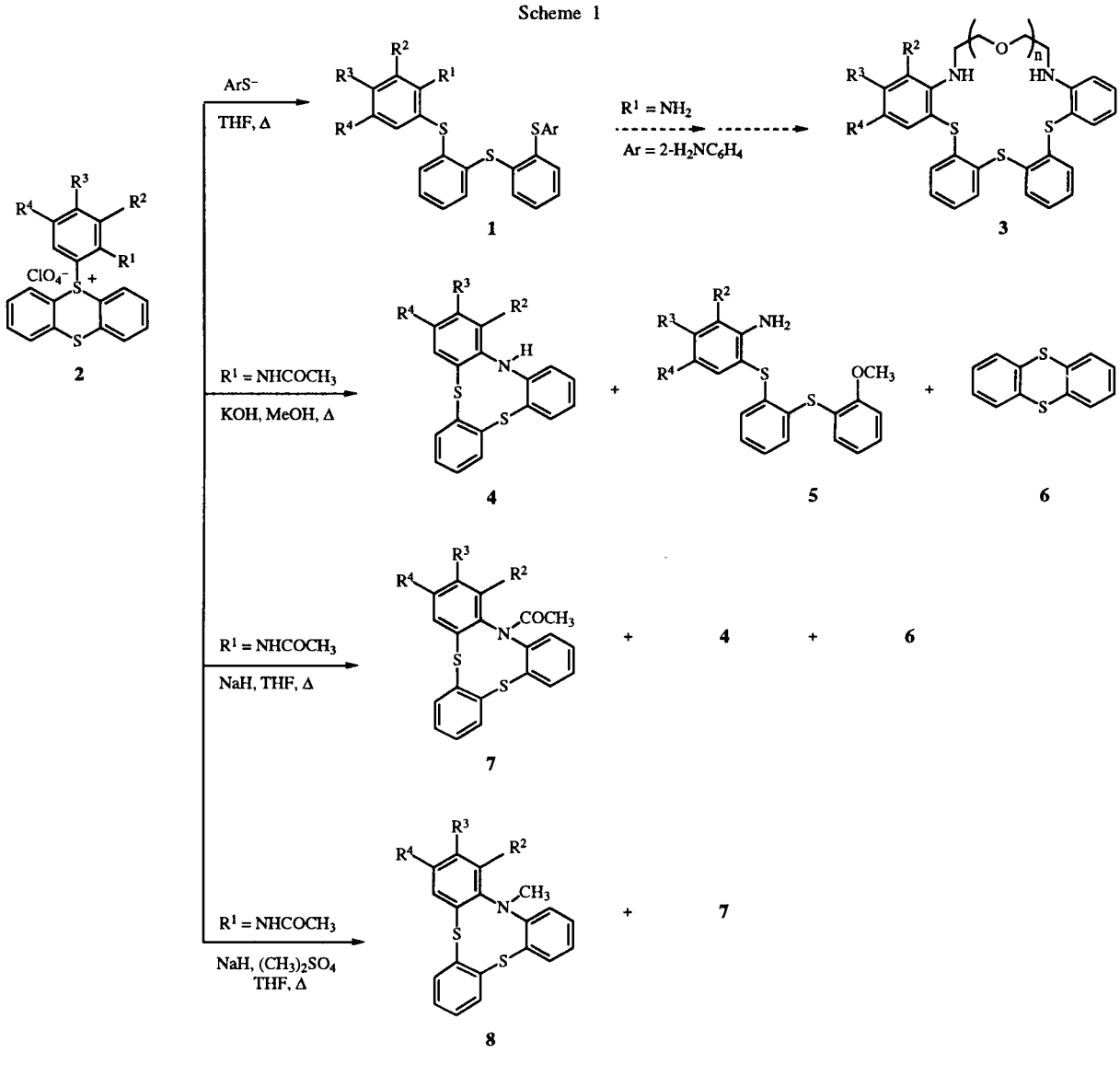
Table 1

Physical and Analytical Data of Compounds **2** ($R^1 = NHCOCH_3$)

Compound	R^2	R^3	R^4	Time hours	Mp (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N	S
2a	H	H	$(CH_3)_3C$	48	142 [a]	95	$C_{24}H_{24}NClO_5S_2$	56.97	4.78	2.77	12.67
								56.87	4.86	2.89	12.52
2b	H	CH_3	CH_3	0.5	244-245 [b]	96	$C_{22}H_{20}NClO_5S_2$	55.28	4.22	2.93	14.41
								55.47	4.35	2.79	13.54
2c	H	CH_3	CH_3CH_2	15	225-227 [c]	90	$C_{23}H_{22}NClO_5S_2$	56.15	4.51	2.85	13.03
								56.25	4.63	2.75	13.16
2d	H	CH_3CH_2	CH_3	24	218-220 [c]	95	$C_{23}H_{22}NClO_5S_2$	56.15	4.51	2.85	13.03
								56.04	4.59	2.91	13.13
2e	H	CH_3CH_2	CH_3CH_2	24	192-194 [c]	97	$C_{24}H_{24}NClO_5S_2$	56.97	4.78	2.77	12.67
								56.86	4.88	2.86	12.61
2f	H	$NHCOCH_3$	CH_3	10	194-195 [b]	94	$C_{23}H_{21}N_2ClO_6S_2$	53.02	4.06	5.38	12.31
								53.12	4.01	5.28	12.20
2g	CH_3	$NHCOCH_3$	H	48	231-232 [b]	98	$C_{23}H_{21}N_2ClO_6S_2$	53.02	4.06	5.38	12.31
								53.11	4.18	5.45	12.17
2h	H	$NHCOCH_3$	H	0.5	195-197 [b]	96	$C_{22}H_{19}N_2ClO_6S_2$	52.12	3.78	5.53	12.65
								52.24	3.88	5.45	12.59

[a] From aqueous ethanol. [b] From ethanol. [c] From methanol.

Scheme 1



^{1}H nmr spectroscopic data in Table 2. Treatment of compounds **2** (R^1 = $NHCOCH_3$) with potassium hydroxide in methanol at reflux gave deacetylated dithiaaza cyclic compounds **4** as major products along with small amounts of 2-(2-aminoarylthio)-2'-methoxydiphenyl sulfides **5** and thianthrene (**6**) except for the reaction with compound **2d** (R^1 = $NHCOCH_3$, R^2 = H, R^3 = CH_2CH_3, R^4 = CH_3) which gave compound **5d** (R^2 = H, R^3 = CH_2CH_3, R^4 = CH_3) as a major product. Reaction conditions and yields of compounds **4**, **5** and **6** are summarized in Table 3 and physical, analytical, ir and ^{1}H nmr spectroscopic data of compounds **4** and **5** are summarized in Table 4 and Table 5, respectively.

The structures of compounds **7** were determined on the basis of the spectroscopic and mass spectral data and elemental analyses. In contrast with ^{1}H nmr data of compounds **4** and compounds **8** (*vide infra*) compounds **7** showed ^{1}H nmr signals of a mixture of two conformational isomers, which were confirmed by X-ray single crystallographic analysis of **7d** (Figure 1). Crystal and refinement parameters for compounds **7d** and atomic coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms of **7d** are listed in Table 6 and 7, respectively. Selected bond distances and angles of conformational isomer **1** of **7d** are tabulated in Table 8 and 9, respectively. Those of conformational isomer **2** of **7d** are tabulated in Table 10 and 11, respectively.

Treatment of compounds **2a**, **2b**, **2d** and **2e** with sodium hydride in tetrahydrofuran for 3 hours at reflux gave, however, compounds **4** with an acetyl group on nitrogen atom **7a**, **7b**, **7c** and **7d**, respectively in good to excellent yields along with a small amount of **6**. Reaction conditions and

Table 2

Ir and ^{1}H nmr Spectral Data of Compounds **2**

Compound	ir (cm^{-1})	^{1}H nmr (DMSO-d_6 + $CDCl_3$) δ (ppm)
2a	3290, 1678, 1095	1.31 (s, 9H, $3CH_3$), 2.10 (s, 3H, CH_3CO), 6.85 (d, 1H, J = 2.0 Hz, NH), 7.24 (d, 1H, J = 9.2 Hz, ArH), 7.68-8.47 (m, 9H, ArH), 10.45 (s, 1H, ArH)
2b	3300, 1667, 1100	2.09 (s, 1H, CH_3CO), 2.30 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 6.95 (s, 1H, ArH), 7.22 (s, 1H, ArH), 7.68-8.08 (m, 8H, ArH), 10.48 (s, 1H, ArH)
2c	3335, 1675, 1100	0.96 (t, 3H, J = 8 Hz, CH_3CH_2), 2.10 (s, 3H, CH_3CO), 2.33 (s, 3H, CH_3), 2.52 (q, 2H, J = 8 Hz, CH_3CH_2), 6.82 (s, 1H, ArH), 7.65-8.16 (m, 8H, ArH), 10.46 (s, 1H, NH)
2d	3340, 1672, 1100	1.19 (t, 3H, J = 8 Hz, CH_3CH_2), 2.10 (s, 3H, CH_3CO), 2.17 (s, 3H, CH_3), 2.65 (q, 2H, J = 8 Hz, CH_3CH_2), 6.96 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.64-8.08 (m, 8H, ArH), 10.50 (s, 1H, NH)
2e	3310, 1667, 1100	0.96 (t, 3H, CH_3CH_2), 1.20 (t, 3H, J = 8 Hz, CH_3CH_2), 2.10 (s, 3H, CH_3CO), 2.48 (q, 2H, J = 8 Hz, CH_3CH_2), 2.72 (q, 2H, J = 8 Hz, CH_3CH_2), 6.84 (s, 1H, ArH), 7.19 (s, 1H, ArH), 7.66-8.13 (m, 8H, ArH), 10.47 (s, 1H, NH)
2f	3490, 3400, 1695, 1671, 1100	2.10 (s, 3H, CH_3CO), 2.19 (s, 6H, $2CH_3CO$), 7.08 (s, 1H, ArH), 7.68-8.05 (m, 10H, ArH), 9.39 (s, 1H, NH)
2g	3455, 3441, 1670, 1100	2.15 (s, 3H, CH_3CO), 2.20 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 7.10 (d, 1H, J = 8.9 Hz, ArH), 7.70-8.00 (m, 9H, ArH), 9.55 (s, 1H, ArH), 10.23 (s, 1H, NH)
2h	3450, 3400, 1670, 1100	2.30 (s, 6H, $2CH_3CO$), 7.24 (d, 1H, J = 9.4 Hz, ArH), 7.47-8.15 (m, 9H, ArH), 10.51 (s, 1H, NH), 10.80 (s, 1H, NH)

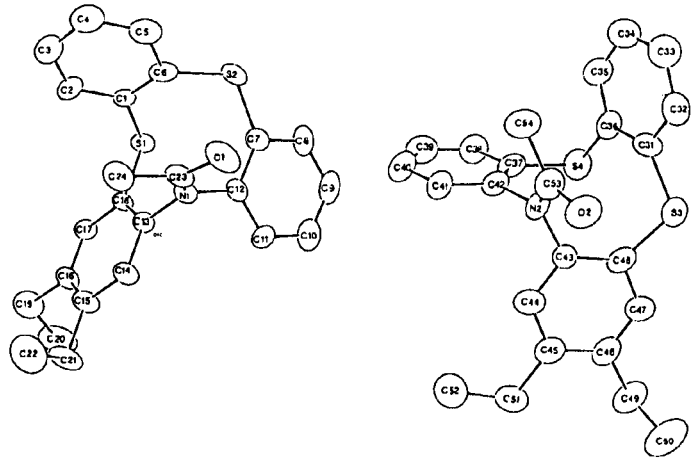
yields of compounds **6** and **7** are summarized in Table 12 and physical, analytical, ir and ^{1}H nmr spectroscopic data of compounds **7** in Table 13. On the other hand, treatment of compounds **2a**, **2b**, and **2e** with sodium hydride in the presence of dimethyl sulfate in tetrahydrofuran at reflux gave compounds **4** with a methyl group on the nitrogen atom, **8a**, **8b**, and **8c** respectively in addition to the corresponding *N*-acetyldithiaaza cyclic compounds **6** and **7**. It is noteworthy that under the same conditions compound **2h** gave an analogous compound **8d** having a *N*-methylacetamido group originated from acetylation of the acetamido group of **2h**. Reaction conditions and yields of compounds **7** and **8** are summarized in Table 14. Physical, analytical, ir and ^{1}H nmr spectroscopic data of compounds **8** are summarized in Table 15.

Table 3

Reaction Condition and Yields of Compounds **4**, **5** [a] and **6**

Compound mmoles	KOH mmoles	MeOH ml	Time hours		Yield [b] %				
2a 0.909	9.09	50	19	**4a**	75	**5a**	11	**6**	9
2b 1.06	10.6	80	108	**4b**	70	**5b**	13	**6**	3
2c 1.08	10.8	80	70	**4c**	69	**5c**	0	**6**	9
2d 0.963	28.9	70	72	**4d**	40	**5d**	43	**6**	5
2e 0.563	5.63	40	65	**4e**	65	**5e**	0	**6**	21
2f 0.735	36.8	60	60	**4f**	43	**5f**	19	**6**	20
2g 1.76	58.7	80	72	**4g**	69	**5g**	9	**6**	10
2h 0.874	69.9	80	206	**4l**	65	**5h**	17	**6**	8

[a] R^2, R^3 and R^4 of compounds **4** and **5** are identical with those of compounds **2** except for R^3 ($R^3 = NH_2$) of **4f**, **4g**, **4h**, **5f**, **5g**, and **5h**. [b] Isolated yields.



Isomer 1 Isomer 2

Figure 1. Molecular structure of compound **7d** with the atomic numbering scheme.

The mechanisms of the formation of *N*-free **4**, *N*-acetyl-**7**, and *N*-alkyldithiaaza cyclic compounds **8** are uncertain. One might conceive a direct nucleophilic attack of amide ions formed by deprotonation of acetamido groups at ipso-position of thianthrene ring, an electron transfer between amide ions and trivalent sulfur cations, or an intramolecular sulfurane formation by bonding between amide ions and sulfur cations. In order to test the possible involvement of a radical mechanism, the reaction of **2b** with sodium hydride was carried out in the presence of tributyltin hydride under nitrogen atmosphere. Addition

Table 4

Physical, Analytical, ir, and ^{1}H nmr Spectroscopic Data of Compounds **4**.

Compound	Mp (°C)	Molecular Formula	Analysis % Calcd./Found C	H	N	S	ir (cm^{-1})	^{1}H nmr ($CDCl_3$) δ (ppm)
4a	106-108 [a]	$C_{22}H_{21}NS_2$	72.69 72.64	5.82 5.89	3.85 3.81	17.64 17.67	3230	1.32 (s, 9H, $(CH_3)_3C$), 6.50-7.93 (m, 11H, ArH), 9.03 (s, 1H, NH)
4b	189-191 [a]	$C_{20}H_{17}NS_2$	71.60 71.65	5.11 5.17	4.18 4.13	19.11 19.05	3230	2.21 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 6.88-7.80 (m, 10H, ArH), 8.63 (s, 1H, NH)
4c	168-169 [a]	$C_{21}H_{19}NS_2$	72.17 72.27	5.48 5.41	4.01 4.07	18.35 18.25	3230	1.18 (t, 3H, J = 8 Hz, CH_3CH_2), 2.27 (s, 3H, CH_3), 2.55 (q, 2H, J = 8 Hz, CH_3CH_2), 6.79-7.76 (m, 10H, ArH), 8.76 (s, 1H, NH)
4d	163-164 [a]	$C_{21}H_{19}NS_2$	72.11 72.27	5.40 5.41	4.01 4.07	18.39 18.25	3229	1.20 (t, 3H, J = 8 Hz, CH_3CH_2), 2.23 (s, 3H, CH_3), 2.60 (q, 2H, J = 8 Hz, CH_3CH_2), 6.57-7.82 (m, 10H, ArH), 8.60 (s, 1H, NH)
4e	144-146 [a]	$C_{22}H_{21}NS_2$	72.69 72.60	5.82 5.72	3.85 3.94	17.64 17.74	3225	1.20 (t, 3H, J = 8 Hz, CH_3CH_2), 1.22 (t, 3H, J = 8 Hz, CH_3CH_2), 2.53 (q, 2H, J = 8 Hz, CH_3CH_2), 2.57 (q, 2H, J = 8 Hz, CH_3CH_2), 6.80-7.77 (m, 10H, ArH), 8.79 (s, 1H, NH)
4f	223-224 [a]	$C_{19}H_{16}N_2S_2$	67.82 67.72	4.79 4.71	8.33 8.39	19.06 19.81	3421, 3323, 3221	2.06 (s, 3H, CH_3), 3.43 (s, br, 2H, NH_2), 6.67-7.75 (m, 10H, ArH), 8.75 (s, 1H, NH)
4g	228-232 [a]	$C_{19}H_{16}N_2S_2$	67.82 67.73	4.79 4.85	8.33 8.39	19.06 19.03	3410, 3335, 3290	2.07 (s, 3H, CH_3), 4.99 (s, br, 2H, NH_2), 6.28-7.42 (m, 10H, ArH), 7.65 (s, 1H, NH)
4h	196-198 [a]	$C_{18}H_{14}N_2S_2$	67.05 67.01	4.38 4.31	8.69 8.75	19.89 19.93	3420, 3396, 3205	3.73 (s, 2H, NH_2), 6.14-7.75 (m, 11H, ArH), 8.87 (s, 1H, NH)

[a] From *n*-hexane.

Table 5

Physical, Analytical, ir, and ^{1}H nmr Spectroscopic Data of Compounds **5**

Compound	Molecular Formula	Analysis % Calcd./Found C	H	N	S	ir (cm^{-1})	^{1}H nmr ($CDCl_3$) δ (ppm)
5a	$C_{24}H_{27}NOS_2$	70.38 70.31	6.64 6.60	3.42 3.47	15.65 15.61	3460, 3360	1.26 (s, 9H, $(CH_3)_3C$), 3.81 (s, br, 2H, NH_2), 3.89 (s, 3H, CH_3O), 6.48-7.53 (m, 11H, ArH)
5b	$C_{21}H_{21}NOS_2$	68.63 68.60	5.76 5.71	3.81 3.89	17.45 17.39	3450, 3361	2.13 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.89 (s, 3H, CH_3O), 3.96 (s, 2H, NH_2), 6.58-7.30 (m, 10H, ArH)
5d	$C_{22}H_{23}NOS_2$	69.25 69.33	6.08 6.15	3.67 3.57	16.81 16.85	3450, 3360	1.20 (t, 3H, J = 8 Hz, CH_3CH_2), 2.20 (s, 3H, CH_3), 2.58 (q, 2H, J = 8 Hz, CH_3CH_2), 4.01 (s, 3H, CH_3O), 4.07 (s, 2H, NH_2), 6.67-7.51 (m, 10H, ArH)
5f	$C_{20}H_{20}N_2OS_2$	65.19 65.10	5.47 5.41	7.60 7.68	17.40 17.35	3462, 3362	2.05 (s, 3H, CH_3), 3.10 (s, br, 4H, $2NH_2$), 3.91 (s, 3H, CH_3O), 6.12 (s, 1H, ArH), 6.71-7.38 (m, 9H, ArH)
5g	$C_{20}H_{20}N_2OS_2$	65.19 65.10	5.47 5.41	7.60 7.70	17.40 17.49	3460, 3365	1.97 (s, 3H, CH_3), 3.85 (s, br, 4H, $2NH_2$), 3.90 (s, 3H, CH_3O), 6.19 (d, 1H, J = 5 Hz, ArH), 6.67-7.39 (m, 9H, ArH)
5h	$C_{19}H_{18}N_2OS_2$	64.38 64.45	5.12 5.04	7.90 7.95	18.09 18.14	3456, 3360	3.69 (s, br, 4H, $2NH_2$), 3.88 (s, 3H, CH_3O), 6.03-6.15 (m, 2H, ArH), 6.71-7.26 (m, 9H, ArH)

of sodium hydride (5 equivalents) to a mixture of compound **2b** (0.628 mmole) and tributyltin hydride (5 equivalents) in tetrahydrofuran (50 ml) gave compounds **6**, *N*-acetyl-2,3,8,9-dibenzo-5,6-(3,4-dimethyl)benzo-1,4-dithia-7-azacyclonona-2,3,8-triene (**7b**) and 2-acetamido 4,5-dimethylphenylthiodiphenyl sulfide (**9**) in 5, 73, 14% yields, respectively (Scheme 2).

Discussion.

The most common approaches employed for the preparation of monocyclic polyhetero ligands involved either the condensations of two-molecule or the intramolecular cyclization of a compound which is formed by a stepwise approach between two different reactants [5]. The yields of those compounds reported are variable depending on the structures but generally low. Although there have been ample examples for the various ring sizes consisting of linkage with different combinations or various heteroatoms, little is known of 9-membered cyclic polyhetero ligands. Those which contain three O [6], two O and one N [6c], one O and two N [6c, 7] one O and two S [8], three N [7c-d, 9] two O and one S [8b] and three S atoms

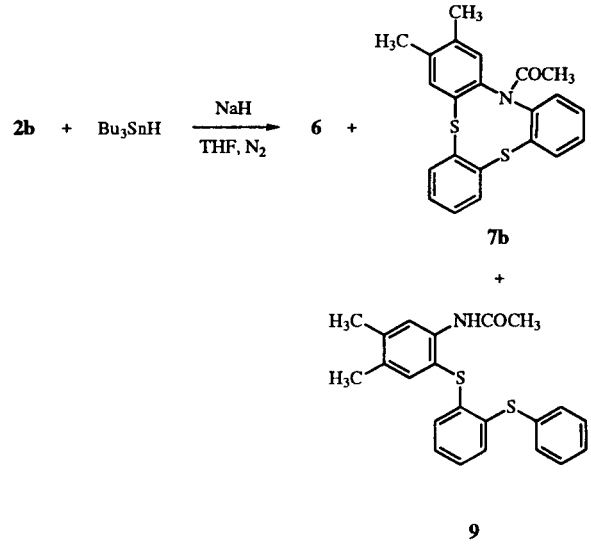
Table 6

Crystal and Refinement Parameters for Compound **7d**

Molecular Formula	$C_{24}H_{23}NOS_2$
Molecular weight	405.6
Color	Colorless
Crystal system	Triclinic
Space group	Pī
a, Å	9.967 (1)
b, Å	14.651 (1)
c, Å	15.133 (2)
α, deg	80.99 (1)
β, deg	72.95 (1)
γ, deg	86.92 (1)
V, Å^3	2083.6
Z	2
ρ calc. g. cm^{-3}	1.29
Crystal size, mm	0.45 x 0.69 x 0.63
Scan type	w/2θ
θ range, deg	1 - 52
μ (M_oK_α)	2.7
N_b of measured reflections	5539
N_b of reflections used $F_o > 3\sigma(F_o)$	4474
N_b of refined parameters	295
R	0.076
Rw	0.074
Diffractometer	Enraf-Nomius CAD 4

[2, 10] in the linkage have been reported. To the best of our knowledge, compounds **4** are the first synthesis of 9-membered cyclic compounds containing two S and one N atom in the linkage. The fact that 2-acetamidoarylthio-

Scheme 2



2'-methoxydiphenyl sulfides **15** have never been isolated from the reactions of **2** with potassium hydroxide in methanol raises a question regarding the time of deacetylation of compounds **2** (R^1 = $NHCOCH_3$) in the course of the formation of compounds **4** and **5**. Since only unreacted compound **7b** was quantitatively recovered from treatment of **7b** with methanolic potassium hydroxide under the similar conditions as in the reactions listed in

Table 7

Positional and Equivalent Isotropic Thermal Parameters of Nonhydrogen Atoms for **7d**

Atom	X	Y	Z	B_{eq} (Å^2)	Atom	X	Y	Z	B_{eq} (Å^2)
S1	0.5961	0.4572	0.1508	3.9	S3	0.9150	1.0989	-0.3633	5.2
S2	0.5595	0.6405	-0.0109	5.8	S4	1.0372	0.8920	-0.2866	4.3
O1	0.6307	0.7949	0.1132	6.2	N2	1.1575	1.0687	-0.2525	2.9
N1	0.6969	0.6506	0.1577	3.5	O2	1.0638	1.2103	-0.2350	4.3
C1	0.4460	0.5327	0.1663	3.3	C31	0.8544	1.0400	-0.2487	3.5
C2	0.3375	0.5120	0.2460	5.5	C32	0.7423	1.0847	-0.1909	4.8
C3	0.2156	0.5680	0.2633	6.4	C33	0.6706	1.0396	-0.1027	5.4
C4	0.2069	0.6454	0.1967	6.7	C34	0.7120	0.9504	-0.0697	5.5
C5	0.3183	0.6663	0.1178	5.7	C35	0.8262	0.9080	-0.1280	4.4
C6	0.4405	0.6093	0.1005	4.4	C36	0.8977	0.9519	-0.2163	3.5
C7	0.7337	0.6323	-0.0073	4.3	C37	1.1663	0.8999	-0.2294	3.1
C8	0.8287	0.6165	-0.0927	5.3	C38	1.2245	0.8166	-0.1969	4.5
C9	0.9750	0.6144	-0.1049	7.1	C39	1.3284	0.8179	-0.1523	4.8
C10	1.0248	0.6217	-0.0304	6.9	C40	1.3738	0.9028	-0.1395	4.4
C11	0.9327	0.6364	0.0540	5.0	C41	1.3157	0.9863	-0.1720	3.9
C12	0.7901	0.6412	0.0671	4.1	C42	1.2116	0.9831	-0.2163	3.0
C13	0.7088	0.5801	0.2326	3.1	C43	1.1969	1.0915	-0.3537	2.8
C14	0.7649	0.6027	0.3009	4.1	C44	1.3396	1.1022	-0.3998	3.3
C15	0.7779	0.5352	0.3746	4.2	C45	1.3906	1.1197	-0.4974	3.5
C16	0.7365	0.4470	0.3785	4.4	C46	1.2897	1.1254	-0.5476	4.0
C17	0.6814	0.4226	0.3090	3.8	C47	1.1495	1.1160	-0.5026	4.1
C18	0.6672	0.4895	0.2366	3.2	C48	1.0990	1.0999	-0.4042	3.8
C19	0.7483	0.3678	0.4573	6.6	C49	1.3344	1.1354	-0.6559	5.6
C20	0.8994	0.3269	0.4314	9.2	C50	1.3151	1.2331	-0.7008	7.6
C21	0.8338	0.5679	0.4476	6.1	C51	1.5475	1.1318	-0.5482	4.7
C22	0.7314	0.6264	0.5032	11.6	C52	1.6402	1.1213	-0.4832	5.5
C23	0.6213	0.7297	0.1754	4.2	C53	1.0882	1.1325	-0.1991	3.7
C24	0.5197	0.7332	0.2700	5.2	C54	1.0380	1.1048	-0.0937	4.1

Table 8

Selected Bond Distances (Å) for **7d**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C48	S3	1.755	S4	C31	2.78
S3	C31	1.759	S4	C35	2.72
C48	C31	2.91	S4	C37	1.767
C37	S4	1.767	C37	C42	1.384
S4	C36	1.769	S4	C42	2.78
C37	C36	2.70	S4	C38	2.71
C43	N2	1.454	N2	C42	1.431
N2	C42	1.431	N2	C41	2.43
C43	C42	2.45	N2	C37	2.44
N2	C53	1.357	N2	C43	1.454
C43	C53	2.43	N2	C44	2.43
C42	N2	1.431	N2	C48	2.50
N2	C53	1.357	S3	C48	1.755
C42	C53	2.46	S3	C43	2.85
S3	C31	1.759	S3	C47	2.64
C31	C36	1.400	O2	C53	1.228
C3	C36	2.82	C53	N2	1.357
S3	C32	2.65	O2	N2	2.25
S4	C36	1.769	N2	C53	1.357
			N2	C54	2.47

Table 3, deacetylation of compounds **2** (R^1 = $NHCOCH_3$) is believed to occur prior to the cyclization leading to compounds **4**. Therefore the mechanism for the formation of compounds **4** is proposed by either a nucleophilic attack of amide ion **10**, which is generated by an addition-elimination of methoxide ion to the carbonyl of the acetamido group, at ipso-position of thianthrene ring involving a Meisenheimer complex intermediate **11a** [11] or a direct displacement of sulfide without involvement of the aromatic π electrons (**11b**) [12] (Scheme 3). Analogous mechanisms have been proposed for the Smiles rearrangement, which normally involves amide ions as nucleophiles [13] and for the reaction of

Table 9

Selected Bond Angles (deg) for **7d**

Atom 1	Atom 2	Atom 3	Angle
C48	S3	C31	111.9
C37	S4	C36	99.7
C43	N2	C42	115.9
C43	N2	C53	119.4
C42	N2	C53	124.2
S3	C31	C36	125.8
S3	C31	C32	113.8
C36	C31	C32	120.1
S4	C36	C31	121.9
S4	C36	C35	118.5
S4	C37	C42	123.2
S4	C37	C38	117.0
N2	C42	C41	118.2
N2	C42	C37	120.5
N2	C43	C44	116.8
N2	C43	C48	122.7
S3	C48	C43	129.3
S3	C48	C47	112.7

Table 10

Selected Bond Distances (Å) for **7d**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S18	S1	1.784	S2	C1	2.84
S1	C1	1.792	S2	C7	1.75
C18	C1	2.72	C7	C12	1.424
C6	S2	1.761	S2	C12	2.88
S2	C7	1.750	C7	C8	1.404
C6	C7	2.91	S2	C8	2.64
C13	N1	1.438	N1	C11	2.43
N1	C12	1.435	N1	C7	2.47
C13	C12	2.43	C14	N1	2.45
N1	C23	1.367	N1	C18	2.46
C13	C23	2.44	S1	C18	1.784
C12	C23	2.45	S1	C17	2.73
S1	C1	1.792	S1	C13	2.79
C1	C6	1.390	C23	O1	1.217
S1	C6	2.78	N1	O1	2.24
S1	C2	2.71	C23	C24	1.498
C6	C2	2.41	N1	C24	2.48
S2	C5	2.66			

Table 11

Selected Bond Angles (deg) for **7d**

Atom 1	Atom 2	Atom 3	Angle
C18	S1	C1	99.1
C6	S2	C7	111.8
C13	N1	C12	115.7
C13	N1	C23	121.0
C12	N1	C23	122.1
S1	C1	C6	121.4
S1	C1	C2	117.2
S2	C6	C5	113.3
S2	C6	C1	128.1
S2	C7	C12	129.7
S2	C7	C8	112.9
C12	C7	C8	117.4
N1	C12	C11	119.9
N1	C12	C7	119.6
C14	C13	N1	119.2
N1	C13	C18	120.7
S1	C18	C17	118.7
S1	C18	C13	121.8

Table 12

Reaction Conditions and Yields of Compounds **6** and **7**

Compound mmoles	NaH [a] mmoles	THF [b] ml	Time hours		Yield [c] %		
2a 0.217	1.08	30	2	**6**	21	**7a**	68
2b 0.238	1.17	50	3	**6**	3	**7b**	96
2d 0.386	1.92	40	2	**6**	12	**7c**	83
2e 0.296	1.46	60	3	**6**	16	**7d**	78

[a] Sodium hydride. [b] Tetrahydrofuran. [c] Isolated yields.

Scheme 3

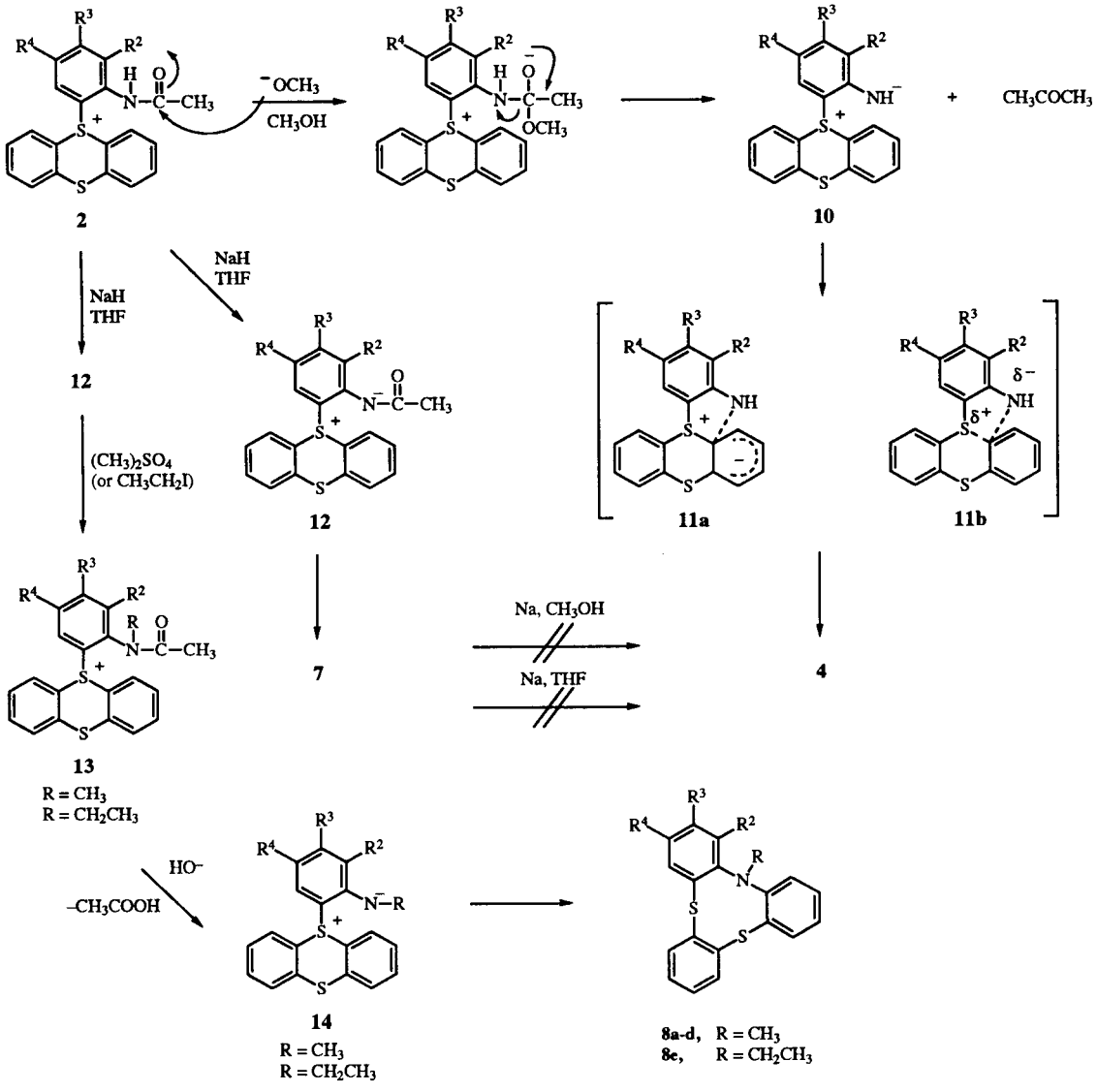


Table 13

Physical, Analytical, ir, and ^{1}H nmr Spectroscopic Data of Compounds **7**

Compound	Mp (°C)	Molecular Formula	Analysis % Calcd./Found C	H	N	S	ir (cm^{-1})	^{1}H nmr (DMSO-d_6 + $CDCl_3$) δ (ppm)
7a	288-290 [a]	$C_{24}H_{23}NOS_2$	71.08 71.01	5.72 5.75	3.45 3.39	15.81 15.86	1670	1.19 (s, 3H, CH_3CO), 1.13 and 1.33 (s, 9H $(CH_3)_3C$), 6.91-7.56 (m, 11H, ArH)
7b	236-237 [b]	$C_{22}H_{19}NOS_2$	69.99 70.04	5.07 4.99	3.71 3.75	16.90 17.07	1675	1.36 and 1.37 (s, 3H, CH_3O), 2.11 and 2.19 (s, 3H, CH_3), 2.19 and 2.24 (s, 3H, CH_3), 6.75-7.60 (m, 10H, ArH)
7c	259-261 [c]	$C_{23}H_{21}NOS_2$	70.55 70.49	5.40 5.33	3.58 3.62	16.38 16.43	1673	1.09 and 1.16 (t, 3H, J = 8 Hz, CH_3CH_2), 1.13 and 1.36 (s, 3H, CH_3CO), 2.16 and 2.24 (s, 3H, CH_3), 2.48 and 2.57 (q, 2H, J = 8 Hz, CH_3CH_2), 6.74-7.62 (m, 10H, ArH)
7d	191-192 [c]	$C_{24}H_{23}NOS_2$	71.08 71.00	5.72 5.68	3.45 3.53	15.81 15.76	1678	1.09-1.36 (m, 9H, $2CH_3CH_2$, CH_3CO), 2.45-2.72 (m, 4H, $2CH_3CH_2$), 6.75-7.61 (m, 10H, ArH)

[a] From a mixture of *n*-hexane and ethyl acetate. [b] From *n*-hexane. [c] From a mixture of *n*-hexane and methylene chloride.

Table 14

Reaction Conditions and Yields of Compounds **6**, **7**, and **8**

Compound mmoles	Base [a] mmoles	Solvent [b] ml	Methyl Sulfate mmoles	Time hours	Yield [c] %					
2a 0.316	0.63	50	0.63	24	**6**	15	**7a**	43	**8a**	27
2b 0.467	1.4	60	0.94	22	**6**	17	**7b**	34	**8b**	37
2e 0.356	0.83	50	0.72	27	**6**	10	**7d**	35	**8c**	44
2h 0.412	2.5	50	1.65	5	**6**	12	**7e**	27	**8d** [d]	56
2b 0.546	1.6	60	5.46 [e]	7.5	**6**	9	**7b**	63	**8e**	28

[a] Sodium hydride. [b] Tetrahydrofuran. [c] Isolated yields. [d] Acetamido group of **2h** was converted to *N*-methylacetamido group. [e] Ethyl iodide was used instead of dimethyl sulfate.

Table 15

Physical, Analytical, ir and ^{1}H nmr Spectroscopic Data of Compounds **8**

Compound	Mp (°C)	Molecular Formula	Analysis % Calcd./Found C	H	N	S	ir (cm^{-1})	^{1}H nmr ($CDCl_3$) δ (ppm)
8a	90-92 [a]	$C_{23}H_{23}NS_2$	73.17	6.14	3.71	16.98	1583, 1495, 1480,	1.28 (s, 9H, $(CH_3)_3C$), 2.27 (s, 3H,
			73.10	6.19	3.76	16.95	1471, 755	NCH_3), 6.73-7.46 (m, 11H, ArH)
8b	114-116	$C_{21}H_{19}NS_2$	72.17	5.48	4.01	18.35	1581, 1469, 1450,	2.15 (s, 6H, $2CH_3$), 2.84 (s, 3H, NCH_3),
	[a]		72.10	5.43	4.08	18.39	759	6.65 (s, 1H, ArH), 6.92-7.43 (m, 9H, ArH)
8c	150-151	$C_{23}H_{23}NS_2$	73.17	6.14	3.71	16.98	1580, 1486, 1460,	1.10 (t, 3H, J = 8 Hz, CH_3CH_2), 1.19 (t,
	[a]		73.11	6.19	3.75	16.95	1450, 739	3H, J = 8 Hz, CH_3CH_2), 2.52 (q, 2H, J = 8 Hz, CH_3CH_2), 2.55 (q, 2H, J = 8 Hz, CH_3 CH_2), 6.68 (s, 1H, ArH), 6.82-7.43 (m, 9H, ArH)
8d	178-180	$C_{22}H_{20}N_2OS_2$	67.32	5.14	17.14	16.33	1659, 1580, 1469,	1.86 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 3.22
	[b]		67.39	5.14	7.04	16.43	735	(s, 3H, CH_3), 6.72 (s, 1H, ArH), 6.81-7.45 (m, 10H, ArH)
8e	188-190	$C_{22}H_{21}NS_2$	72.69	5.82	3.85	17.64	1460, 1449, 753	0.59 (t, 3H, J = 8 Hz, CH_3CH_2), 2.14 (s,
	[b]		72.61	5.89	3.79	17.71		3H, CH_3), 2.18 (s, 3H, CH_3), 3.24 (q, 2H, J = 8 Hz, CH_3CH_2), 6.61 (s, 1H, ArH), 6.87-7.46 (m, 9H, ArH)

[a] From a mixture of *n*-hexane and methylene chloride. [b] From *n*-hexane.

3-acetamido-5-chloro-2-(5-chloro-3-nitro-2-pyridylsulfonyl)pyridine with potassium hydroxide in methanol at reflux [14].

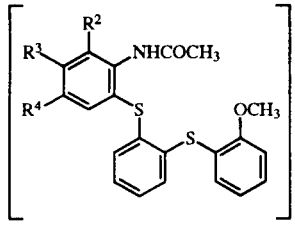
Similarly the formation of *N*-acetyldithiaaza cyclic compounds **7** by treament of compounds **2** (R^1 = $NHCOCH_3$) with sodium hydride in tetrahydrofuran at reflux (Table 12) can be explained by assuming the intermediacy of *N*-acylamide ion **12** formed by deprotonation of the acetamido groups of **2** (Scheme 3). Compound **7b** was not hydrolyzed by either sodium hydride or sodium methoxide in methanol at reflux and was recovered in over 90% yields. These results coupled with the recovery of **7b** from treatment with methanolic potassium hydroxide clearly indicate that compounds **7** are not intermediates for the formation of compounds **4**.

The formation of *N*-alkyldithiaaza cyclic compounds **8** (Table 14) can be rationalized on the basis of the formation of *N*-alkyl amide ions **14**, presumably formed by hydrolysis of *N*-alkylacetamido groups of compounds **13** with hydroxide ion formed by incompletely dried water in the solvent with sodium hydride. The formation of compounds **8** *via* intermediates **13** was confirmed by treatment of independently synthesized 5-[2-(*N*-methyl)acetamido-4,5-dimethylphenyl]thianthreniumyl perchlorate **13** (R = CH_3, R^2 = H, R^3 = R^4 = CH_3) with sodium hydride and dimethyl sulfate in tetrahydrofuran under the same conditions as in the reaction of compound **2b** described. The reaction with independently synthesized compound **13** gave compounds **8b** in 78% yield, whereas that with compound **2b** gave compounds **7b** and **8b** in 34

and 37% yields, respectively (Table 14). It is noteworthy that the sum of yields of **7b** and **8b** (71%) is close to the yield of 78% obtained from the reaction with compound **13** (R = CH_3, R^2 = H, R^3 = R^4 = CH_3). This result supports the existence of *N*-acetamide ions **12** which undergo either cyclization reactions to give compounds **7** or nucleophilic substitution reactions in the presence of dimethyl sulfate or ethyl iodide to give compounds **13** which are subsequently hydrolyzed to give compounds **8** *via* intermediates **14**.

The proposed mechanism for the formation of either compounds **4**, **7**, or **8** from acetamido compounds **2** is similar to those for Smiles rearrangement [13] except for one difference. That is, Smiles rearrangement produces normally sulfinates from sulfones whereas a kind of aryl sulfides **4**, **7**, and **8** are produced from sulfonium ions **10**, **12**, and **14**, respectively in our hand. In this regard, the reactions leading to compounds **4**, **7**, and **8** are considered a new type of Smiles rearrangement involving sulfonium ions.

The formation of compounds **5** can be rationalized on the basis of nucleophilic attack of methoxide ion at ipso-position of the thianthrene ring (Table 3), which is analogous to the mechanism of the formation of 2-arylthiophenyl-2'-biphenyl sulfide from the reaction of **2** (R^1 = R^2 = R^4 = H, R^3 = CH_3) with phenylmagnesium chloride and 2-phenylthiodiphenyl sulfide and 2-butyl-2'-phenylthiodiphenyl sulfide from the reaction of **2** (R^1 = R^2 = R^4 = H, R^3 = CH_3) with butylmagnesium chloride proposed by Shine and coworkers [15]. However, it is uncertain whether the precursors of compounds **5** are compounds **2** (R^1 = NH_2) or compounds **15** since synthesis of **2** (R^1 = NH_2) has been unsuccessful.



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One might conceive a sulfurane mechanism for the formation of compounds **4**, **7**, and **8**. However, the mechanism might not be appropriate because of an unfavorable conformational feature. Compound **2b** was subjected to X-ray single crystallographic analysis. The molecular structure of **2b** is shown in Figure 2. Crystal and refinement parameters for compound **2b** and its atomic coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms are listed in Table 16 and 17, respectively. Selected bond distances and bond angles of **2b** are tabulated in Table 18, and 19, respectively. The crystal structure reveals that the distance between trivalent sulfur and nitrogen atom of acetamido group is calculated to be about 3 Å [16] which is much longer than that (1.6-2.6 Å) of the apical bond of the stable sulfuranes [17]. We do not know the nearest distance between trivalent sulfur and nitrogen atoms in compound **2b** in the solution phase. Nevertheless, it is expected that the

Table 16

Crystal and Refinement Parameters for Compound **2b**

Molecular Formula	$C_{22}H_{20}NClO_2S_5$
Molecular weight	478.0
Color	Colorless
Crystal system	Monoclinic P
Space group	p^2_1/n
a, Å	12.262 (2)
b, Å	15.046 (2)
c, Å	12.284 (2)
α, deg	90.00
β, deg	104.21 (3)
γ, deg	90.00
V, Å^3	2199.2 (1)
Z	4
ρ calc. g. cm^{-3}	1.44
Crystal size, mm	0.9 x 0.38 x 0.16
Scan type	θ/2θ
θ range, deg	1-46
μ (M_oK_α)	2.7
N_b of measured reflections	3282
N_b of reflections used $I \geq 3\sigma$ (I)	1828
N_b of refined parameters	280
R	0.089
Rw	0.087
Diffractometer	Enraf-Nomius CAD 4

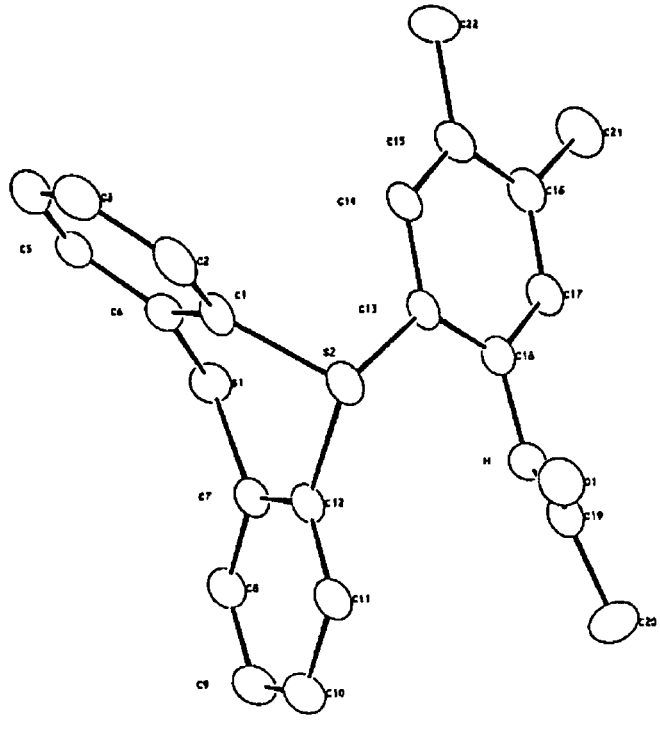


Figure 2. Molecular structure of compound **2b** with the atomic numbering scheme.

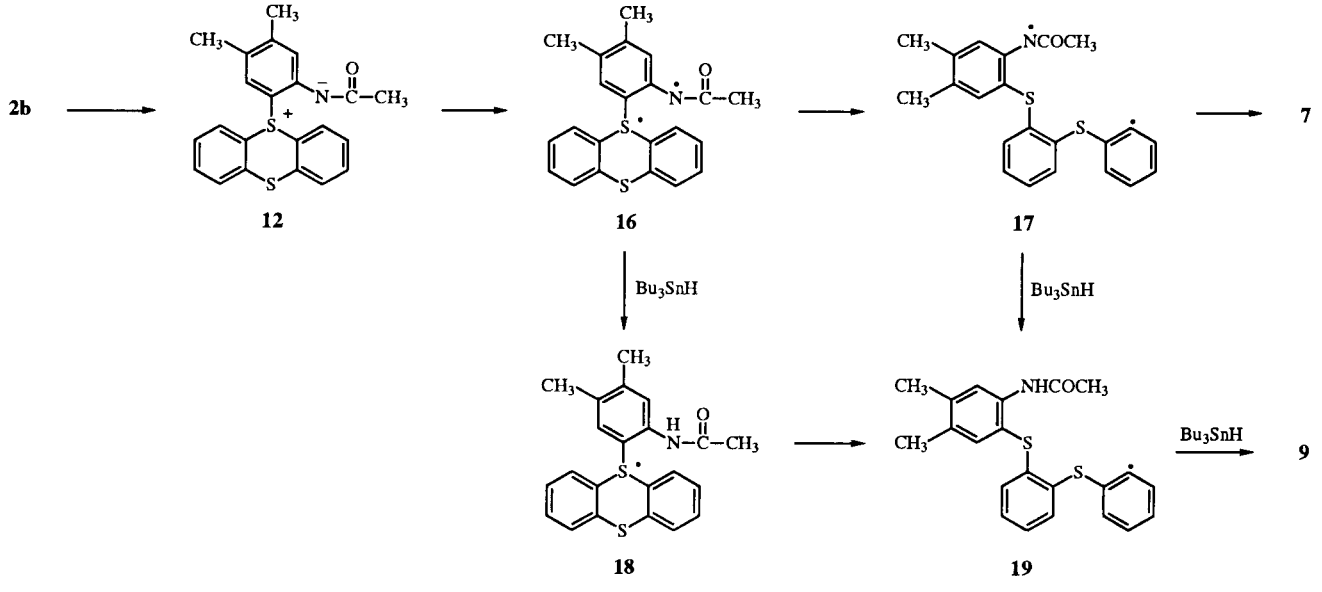
Table 17

Positional and Equivalent Isotropic Thermal Parameters of Nonhydrogen Atoms for **2b**

Atom	X	Y	Z	B_{eq} (Å^2)	Atom	X	Y	Z	B_{eq} (Å^2)
CL	0.2351	0.1718	0.7695	4.63	C8	0.0164	0.1879	0.3765	4.3
S1	0.1102	0.3040	0.2570	3.82	C9	-0.0271	0.1047	0.3954	5.1
S2	0.0711	0.1487	0.0677	3.40	C10	-0.0371	0.0358	0.3185	5.4
O1	-0.1479	0.0757	-0.0308	4.5	C11	-0.0069	0.0492	0.2173	4.3
O2	0.1867	0.1651	0.6540	11.5	C12	0.0324	0.1330	0.1971	3.4
O3	0.1616	0.1308	0.8289	5.1	C13	-0.0066	0.2447	0.0022	3.0
O4	0.3416	0.1338	0.8006	9.4	C14	0.0521	0.3027	-0.0517	3.4
O5	0.2465	0.2635	0.7968	8.3	C15	0.0015	0.3800	-0.1022	3.9
N	-0.1866	0.2041	0.0489	3.4	C16	-0.1106	0.3993	-0.0977	3.8
C1	0.2053	0.1979	0.1202	3.6	C17	-0.1676	0.3396	-0.0454	3.6
C2	0.2931	0.1644	0.0794	5.0	C18	-0.1187	0.2608	0.0020	3.2
C3	0.3987	0.2088	0.1134	5.8	C19	-0.2040	0.1165	0.0225	3.9
C4	0.4109	0.2821	0.1850	5.7	C20	-0.2979	0.0735	0.0643	5.4
C5	0.3223	0.3118	0.2288	4.5	C21	-0.1699	0.4838	-0.1484	5.4
C6	0.2192	0.2675	0.1976	3.6	C22	0.0672	0.4422	-0.1613	5.4
C7	0.0488	0.2016	0.2759	3.4					

bond formation between trivalent sulfur and nitrogen atoms to become a trigonal bipyramid [17] by approaching of the nitrogen atom from the apical position would be difficult because of rigid geometry of thianthrene molecule and angle strains of sulfurane associated with the phenyl group having an acetamido group. Indeed no sulfurane associated with four membered transition state in which a carbon-carbon bond of phenyl ring becomes a bond of the four membered transition state has been reported. Therefore, the involvement of a sulfurane mechanism in the cyclizations of compounds **2** (R^1 = $NHCOCH_3$) is highly unlikely. However, one cannot rule out a radical mechanism involving a sulfuranyl radical **16** formed by an electron transfer between amide ion and trivalent sulfur cation of **12** in view of the isolation of compound **9** in 14% yield by addition of sodium hydride in a mixture of compound **2b** and tributyltin hydride at reflux. Since no compound **9** was isolated in the absence of tributyltin hydride coupled with the formation of compounds **7** in moderate to excellent yields (Table 12) it might be reasonable to assume that compounds **7** would be also formed by an intramolecular coupling reaction of diradical **17** (Scheme 4). The formation of **9** might be attributable to a hydrogen atom transfer from tributyltin hydride to arylthiophenyl radical **19** which could be formed by a hydrogen atom transfer to either diradical **17** or a sulfuranyl radical **18** presumably formed by a hydrogen atom transfer to amidyl radical of **16**. Further study is needed to delineate the mechanism The structure of compound **9** was determined based on mass spectral data and microanalyses in addition to comparison with the authentic sample which could be obtained

Scheme 4



in 11% yield by treatment of **2b** with lithium aluminum hydride in tetrahydrofuran at room temperature.

Table 18

Selected Bond Distances (Å) for **2b**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1	C2	1.389	S2	C1	1.777
S1	C6	1.761	N	C18	1.410
C1	C6	1.395	C13	C18	1.394
S1	C7	1.755	O1	C19	1.226
S2	C12	1.783	C15	C22	1.530
C7	C12	1.394	C16	C21	1.521
S2	C13	1.808	C19	C20	1.516
C13	C14	1.397			

Table 19

Selected Bond Angles (deg) for **2b**

Atom 1	Atom 2	Atom 3	Angles
C6	S1	C7	100.1
C1	S2	C12	99.0
C12	S2	C13	106.0
C18	N	C19	124.2
S2	C1	C2	116.6
C2	C1	C6	122.8
S1	C6	C1	122.5
C1	C6	C5	119.7
S1	C7	C8	117.9
C8	C7	C12	118.7
S2	C12	C7	119.8
C7	C12	C11	122.9
N	C19	C20	114.9
N	C18	C17	116.7
O1	C19	C20	122.7

EXPERIMENTAL

General Procedure for the Preparation of 5-(Aryl)thianthreniumyl Perchlorates **2a-h**.

To a solution of thianthrene cation radical perchlorate (3 mmoles) in dried acetonitrile (50 ml) was added anilide (1.5 mmoles). The mixture was stirred for an appropriate time and worked up as described in the literature [4]. Consult Table 1 for the reaction times, yields, and analytical data and Table 2 for ir and ^{1}H nmr spectroscopic data of compounds **2**.

General Procedure for the Synthesis of 2,3,8,9-Dibenzo-5,6-(substituted)benzo-1,4-dithia-7-azacyclonona-2,5,8-trienes **4**.

To a solution of compounds **2** (1 mmole) in methanol (40-80 ml) was added solid potassium hydroxide (10 mmoles). The mixture was heated at reflux and then quenched with water (1 ml). After removal of the solvent *in vacuo*, the residue was extracted with methylene chloride (3 x 30 ml). The extracts were washed with water (2 x 30 ml) and dried over magnesium sulfate. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed on silica gel (1.5 x 10 cm). Elution with *n*-hexane gave thianthrene (**6**). Elution with a mixture of *n*-hexane and benzene (1:1) gave compounds **4**. Elution with benzene and subsequently with methylene chloride gave a complex mixture and 2-(2-aminophenylthio)-2'-methoxydiphenyl sulfides **5**, respectively. Consult Table 3 for reaction conditions and yields of compounds **4**, **5**, and **6**, and Table 4 and Table 5 for physical, analytical, ir, and ^{1}H nmr spectroscopic data of compounds **4** and **5**, respectively.

General Procedure for the Synthesis of *N*-Acetyl-2,3,8,9-dibenzo-5,6-(substituted)benzo-1,4-dithia-7-azacyclonona-2,5,8-trienes **7**.

To a solution of compounds **2** (0.2-0.3 mmole) in tetrahydrofuran (50 ml) was added sodium hydride (1-2 mmoles). The mixture was heated for an appropriate time at reflux and then cooled to room temperature, followed by quenching with water (1 ml). After removal of the solvent *in vacuo*, the residue was extracted with methylene chloride (3 x 30 ml). The extracts were dried over magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (1.5 x 10 cm). Elution with *n*-hexane gave **6**. Subsequent elution with ethyl acetate gave compounds **7**. Consult Table 12 for reaction conditions and yields of compounds **9** and **10**, and Table 10 for physical, analytical, ir, and ^{1}H nmr spectroscopic data of compounds **7**.

General Procedure for the Synthesis of *N*-Alkyl-2,3,8,9-dibenzo-5,6-(substituted)benzo-1,4-dithia-7-azacyclonona-2,5,8-trienes **8**.

To a solution of compounds **2** (0.3-0.5 mmole) and dimethyl sulfate (0.6-2 mmoles) (or ethyl iodide, 6 mmoles) in dried tetrahydrofuran (50-60 ml) was added sodium hydride (0.6-2 mmoles). The mixture was heated for several hours at reflux and then cooled to room temperature, followed by quenching with water (1 ml). After removal of the solvent *in vacuo*, the residue was extracted with methylene chloride (3 x 30 ml). The combined extracts were washed with water (2 x 20 ml) and dried over magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (1.5 x 10 cm). Elution with *n*-hexane gave **6**. Elution with methylene chloride gave a complex mixture and subsequent elusion with a mixture of *n*-hexane and ethyl acetate (1:1) gave compounds **7**. Consult Table 14 for reaction conditions and yields of compounds **6**, **7**, and **8**, and Table 15 for physical, analytical, ir, and ^{1}H nmr spectroscopic data of compounds **8**.

Reaction of 5-(2-Acetamido-4,5-dimethylphenyl)thianthreniumyl Perchlorate (**2b**) with Sodium Hydride in the Presence of Tributyltin hydride.

To a solution of compound **2b** (300 mg, 0.628 mmole) and tributyltin hydride (914 mg, 3.14 mmoles) in dried tetrahydrofuran was added sodium hydride (75 mg, 3.1 mmoles). The mixture was heated for 2 hours under nitrogen atmosphere and then cooled to room temperature, followed by quenching with water (2 ml). After removal of the solvent *in vacuo*, the residue was extracted with methylene chloride (3 x 30 ml). The extracts were dried over magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (3 x 5 cm). Elution with *n*-hexane gave a mixture of unreacted tributyltin hydride and hexabutylditin. Elution with methylene chloride gave **6** (7 mg, 5%). Subsequent elution with a mixture of *n*-hexane and ethyl acetate (1:1) gave 2-acetamido-4,5-dimethylphenylthiodiphenyl sulfide (**9**) (34 mg, 14%), which was recrystallized from *n*-hexane: mp 109-110°; ^{1}H nmr (deuteriochloroform): δ 1.98 (s, 3H, CH_3CO), 2.22 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 6.65-7.23 (m, 11H, ArH), 8.21 (s, 1H, NH); ir (neat): 3335, 1685 cm^{-1}; ms: m/z 379 (M^+).

Anal. Calcd. for $C_{22}H_{21}NOS_2$: C, 69.62; H, 5.58; N, 3.69; S, 16.89. Found: C, 69.68; H, 5.51; N, 3.60; S, 16.94.

Elution with ethyl acetate gave **7b** (173 mg, 73%).

Reaction with **2b** with Lithium Aluminum Hydride.

To a solution of compound **2b** (189 mg, 0.377 mmoles) in tetrahydrofuran (30 ml) was added lithium alumium hydride (48 mg, 1.3 mmoles) at room temperature. The mixture was stirred for 20 hours at room temperature, and then quenched with water (0.5 ml). After removal of the solvent *in vacuo*, the residue was extracted with methylene chloride (3 x 30 ml). The combined extracts were washed with water (2 x 20 ml) and dried over magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (1.5 x 3 cm). Elution with a mixture of *n*-hexane and ethyl acetate (3:7) gave **9** (15 mg, 11%).

Reaction of 5-[2-(*N*-Methyl)acetamido-4,5-dimethylphenyl]thianthreniumyl Perchlorate (**14a**) with Sodium Hydride.

To a solution of **14a** (200 mg, 0.407 mmole) in dried tetrahydrofuran (40 ml) was added sodium hydride (49 mg, 2.0 mmoles). The mixture was heated for 4 hours at reflux, and worked up as described for the synthesis of compounds **4**. Chromatography of the reaction mixture on silica gel (1.5 x 7 cm) using *n*-hexane as an eluent gave **6** (6 mg, 7%). Elution with carbon tetrachloride gave *N*-methyl-2,3,8,9-dibenzo-5,6-(3,4-dimethyl)benzo-1,4-dithia-7-azacyclonona-2,5,8-triene (**8b**) (111 mg, 78%). Subsequent elution with a mixture of *n*-hexane and ethyl acetate (1:1) gave an unknown mixture (31 mg).

Single Crystal X-ray Analyses of **2b** and **7d**.

Crystallographic and refinement parameters are summarized in Tables 16 and 6, respectively.

The data were collected on an Enraf-Nomius CAD4 diffractometer using graphite-monochromated M_o-K_α radiation. The structure was solved by direct methods and subsequent Fourier maps. Refinements were carried out by full-matrix least-squares techniques. Non-hydrogen atoms were anisotropically refined. Atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol **IV**, 1974. All Calculations and drawings were performed using a Micro VAX II computer with the SDP system.

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