Synthesis and Structure of 6,7-Dihydro-2,3-disubstituted 5*H*-2a-Thia(2*a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione

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(Received December 23, 1987)

Symmetrical tetraazapentalene derivatives **5** and **6** were synthesized by a convenient one-pot reaction using lithium thioureide/phenacyl chloride/alkyl (or allyl) isothiocyanate system. Unsymmetrical tetraazapentalene derivatives **8** were prepared by the reaction of various isothiocyanates with thiadiazolopyrimidine derivatives **7** which were derived from symmetrical tetraazapentalene derivatives. The structure of **5c** was determined by a single crystal X-ray diffraction.

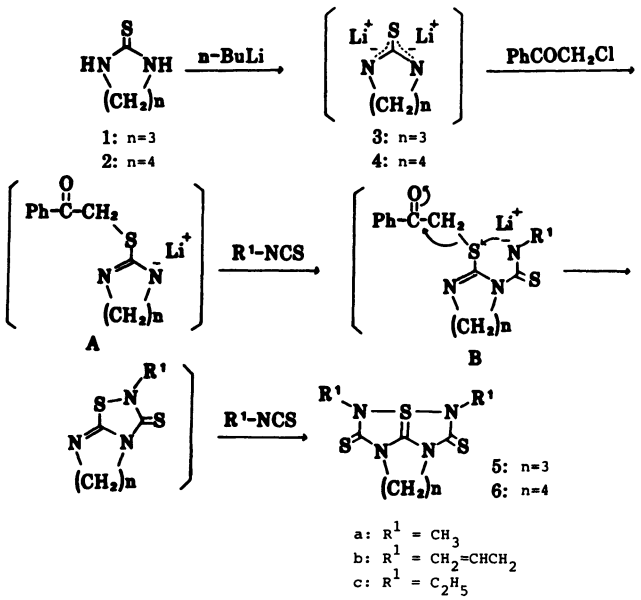
Chemistry of π-hypervalent heterocyclic systems related to 6a-thia(S^{IV})pentalene has been of considerable current interest, and several systems containing S–S^{IV}–S, S–S^{IV}–O, or N–S^{IV}–N bond and 10π-electrons in the framework were synthesized.[1] We have recently reported that the dianion **3** of 3,4,5,6,-tetrahydro-2(1*H*)-pyrimidinethione (**1**) reacted with methyl isothiocyanate to give 6,7-dihydro-2,3-dimethyl-5*H*-2a-thia(*2a*-S^{IV}) -2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4-(2*H*,3*H*)-dithione (**5a**)[2] in low yield. Compounds of this type[3] containing π-hypervalent sulfur and 12π-electrons in the framework are of interest, because the structure, stability, and reactivity should be different from those of the other 6a-thia(S^{IV})pentalene analogs mentioned above. Recently, we have established general preparation of the symmetrical and unsymmetrical tetraazapentalene derivatives reported as preliminary communications.[4] In this paper, we describe the detail of preparation of symmetrical tetraazapentalene derivatives **5** and **6**, the first example of the X-ray crystallographic structure of a new heteropentalene, 6,7-dihydro-2,3-diethyl-5*H*-2a-thia-(*2a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*, 3*H*)-dithione (**5c**), and the smooth conversion of the symmetrical tetraazapentalene derivatives to the unsymmetrical ones **8** via selective elimination of alkyl (or allyl) isothiocyanate followed by 1,3-dipolar cycloaddition.

Results and Discussion

Synthesis of Symmetrical Tetraazapentalene Derivatives. Cyclic thioureas **1** and **2** were treated with two molar equivalents of butyllithium in tetrahydrofuran (THF) at 0 °C under argon. When the resulting dianions **3** and **4** were reacted with a molar equivalent of phenacyl chloride to give intermediate **A**, followed by addition of isothiocyanate (three molar equivalents), the tetraazapentalene derivatives **5** and **6** were obtained as colorless solids in good yields. These compounds are stable under the atmosphere.

The yields of products are shown in Table 1. The structures of **5** and **6** were determined by IR, ^{1}H NMR, ^{13}C NMR, mass spectra, and elemental analyses.

Scheme 1 shows a possible reaction mechanism for the formation of tetraazapentalenes, **5** and **6**. In this reaction, the formation of acetophenone was recognized. The yields of products depended on the ring size of cyclic thiourea and on the bulkiness of the alkyl group of alkyl isothiocyanate. When phenyl or *t*-butyl isothiocyanate was used in this reaction, no tetraazapentalene derivative was produced. The dianion **3**



Scheme 1.

Table 1. Preparation of Tetraazapentalene Derivatives[a]

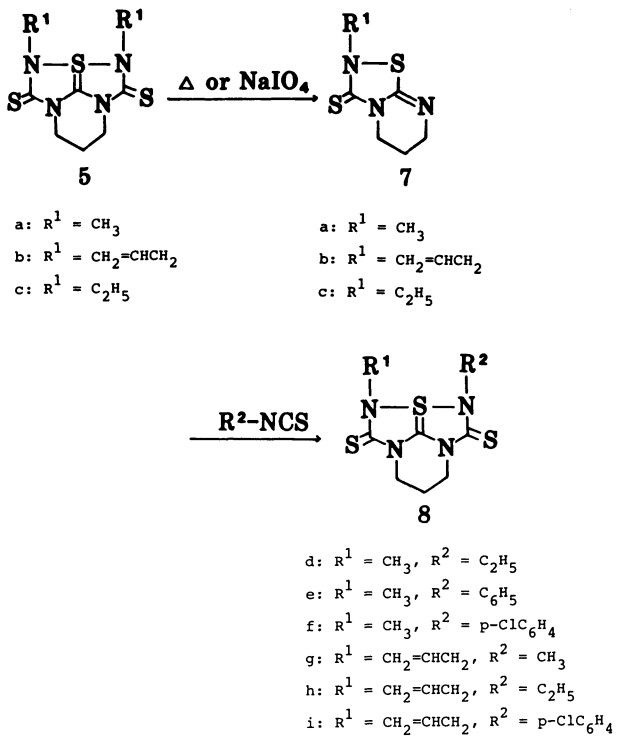
Entry	Dianion	R in R-NCS	Product	Yield/%[b]
1	**3**	CH_3	**5a**	74
2	**3**	CH_2=$CHCH_2$	**5b**	65
3	**3**	C_2H_5	**5c**	64
4	**4**	CH_3	**6a**	27
5	**4**	CH_2=$CHCH_2$	**6b**	9
6	**4**	C_2H_5	**6c**	14

a) The reactions were carried out in tetrahydrofuran at room temperature for 24 h under argon. b) Isolated yield.

derived from the 6-membered ring thiourea **1** gave tetraazapentalene derivatives more effectively than the dianion **4** derived from the 7-membered ring thiourea **2**. On the other hand, when a dianion derived from the 5-membered ring thiourea, 2-imidazolidinethione, was used in this reaction, tetraazapentalene derivative was not obtained. The intermediate derived from the 2-imidazolidinethione could not have favorable conformation for the attack of the nitrogen atom to the sulfur atom.

Synthesis of Unsymmetrical Tetraazapentalene Derivatives. The thermolysis or oxidation reaction of 6,7-dihydro-2,3-dimethyl-5*H*-2a-thia(*2a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**5a**) gave easily 6,7-dihydro-2-methyl-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine-3(2*H*)-thione (**7a**). Furthermore, **7a** was found to undergo a 1,3-dipolar cycloaddition with various isothiocyanates to give unsymmetrical tetraazapentalene derivatives having different groups at 3,4-positions (Scheme 2).

When the compounds **5** were heated at 170 °C under reduced pressure (2 mmHg, 1 mmHg≈133.322 Pa) or treated at room temperature with sodium periodate in methanol, the products **7** were obtained in moderate yields. The yields are shown in Table 2.



Scheme 2.

The thermolysis under reduced pressure (method A) is preferable to the oxidation reaction using $NaIO_4$ (method B) for the preparation of **7**. The structure of **7** was determined by IR, ^{1}H NMR, mass spectra, and elemental analyses. The compound **7** reacted smoothly with the isothiocyanates to give the unsymmetrical tetraazapentalene derivatives **8**. When the reaction of various isothiocyanates (1.5 times molar quantity of **7**) with **7** were carried out in refluxing chloroform for 3 h, the unsymmetrical tetraazapentalene derivatives **8** were obtained in good yields. The yields are shown in Table 3. All compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, UV, mass spectra, and elemental analyses.

Structure of Tetraazapentalene Derivatives. In order to establish the structure of the tetraazapentalene derivatives, a single crystal X-ray diffraction of **5c** was performed. The crystal of **5c** was most suitable for an X-ray diffraction among those of **5**, **6**, and **8**. Figure 1 shows the molecular structure of **5c**. Selected bond lengths and angles are listed in Table 4.

Figure 2 shows the molecular structure of **5c** viewed along the S(2)–C(1) bond and Table 5 shows the distance to the plane from the atoms in the molecule. The X-ray crystallographic analysis provides the following structural characteristics: (i) The S(1)–C(2) bond length [1.705 Å] is fairly shorter than the usual S(6a)–C(3) bond length [1.75 Å][5] of 6a-thia(S^{IV})pentalene analogs; (ii) the S(1)–N(1) [1.927 Å] and S(1)–N(2) [1.891 Å] bond lengths differ from each

Table 2. Preparation of Thiadiazolopyrimidine Derivatives **7**

	R^1	Method	Product	Yield/%
5a	CH_3	A[a]	**7a**	69
5a	CH_3	B[b]	**7a**	33
5b	CH_2=$CHCH_2$	A	**7b**	75
5b	CH_2=$CHCH_2$	B	**7b**	27
5c	CH_3CH_2	A	**7c**	62
5c	CH_3CH_2	B	**7c**	13

a) The compound was heated at 170 °C under reduced pressure (2 mmHg). b) Sodium periodate was used as an oxidizing agent.

Table 3. Preparation of Unsymmetrical Tetraazapentalene Derivatives **8**[a]

Entry	Thiadiazolopyrimidine	R^2 in R^2-NCS	Product	Yield/%[b]
1	**7a**	CH_3CH_2	**8d**	84
2	**7a**	C_6H_5	**8e**	85
3	**7a**	*p*-ClC_6H_4	**8f**	63
4	**7b**	CH_3	**8g**	63
5	**7b**	CH_3CH_2	**8h**	86
6	**7b**	*p*-ClC_6H_4	**8i**	66

a) The reactions were carried out in refluxing chloroform for 3 h. b) Isolated yield.

other, and it means that **5** has an unsymmetrical structure; (iii) the S–N bond length [1.91 Å, average] is 9% longer than the usual S–N single bond length [1.74 Å];[6] the external C=S double bond length [1.68 Å, average] is 4% longer than the usual C=S double bond length [1.61 Å];[6] and (v) the tetraazapentalene framework can be regarded as planar, because the maximum distance between the framework atoms and the plane is only 0.013 Å as seen in Table 5. Figure 3 shows the drawing of the molecular packing.

In spite that the tetraazapentalene **5c** formally has four tertiary nitrogen atoms, the framework was elucidated to be planar by X-ray crystallographic analysis. This fact indicates much contribution from polar resonance contributors to the electronic structure of **5** as illustrated in Scheme 3. The extension of the external C=S double bond length is due to such polar resonance contributors. In accord with the planarity of the framework, the four nitrogen atoms may have nature of the sp^2 configuration. In the conjugated π-system, twelve π-electrons are well delocalized on the tetraazapentalene framework.

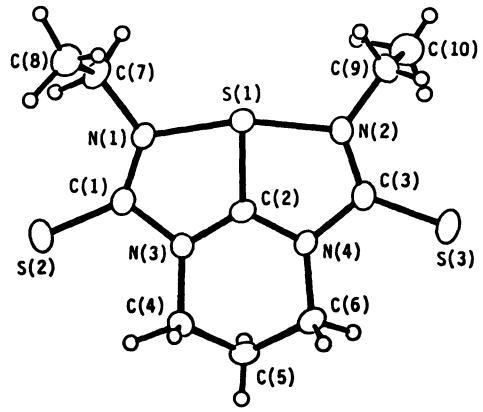


Fig. 1. Molecular structure of **5c** with numbering scheme.

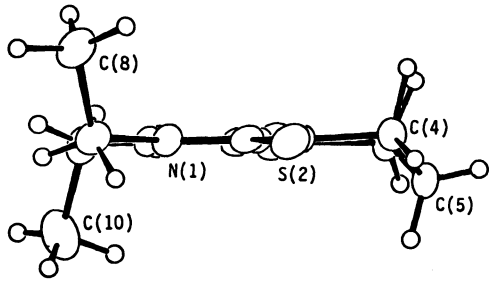


Fig. 2. Molecular structure of **5c** viewed along the S(2)–C(1) bond.

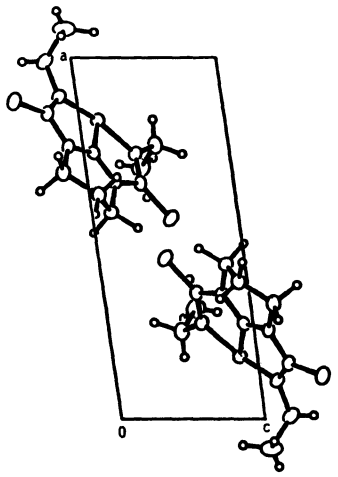


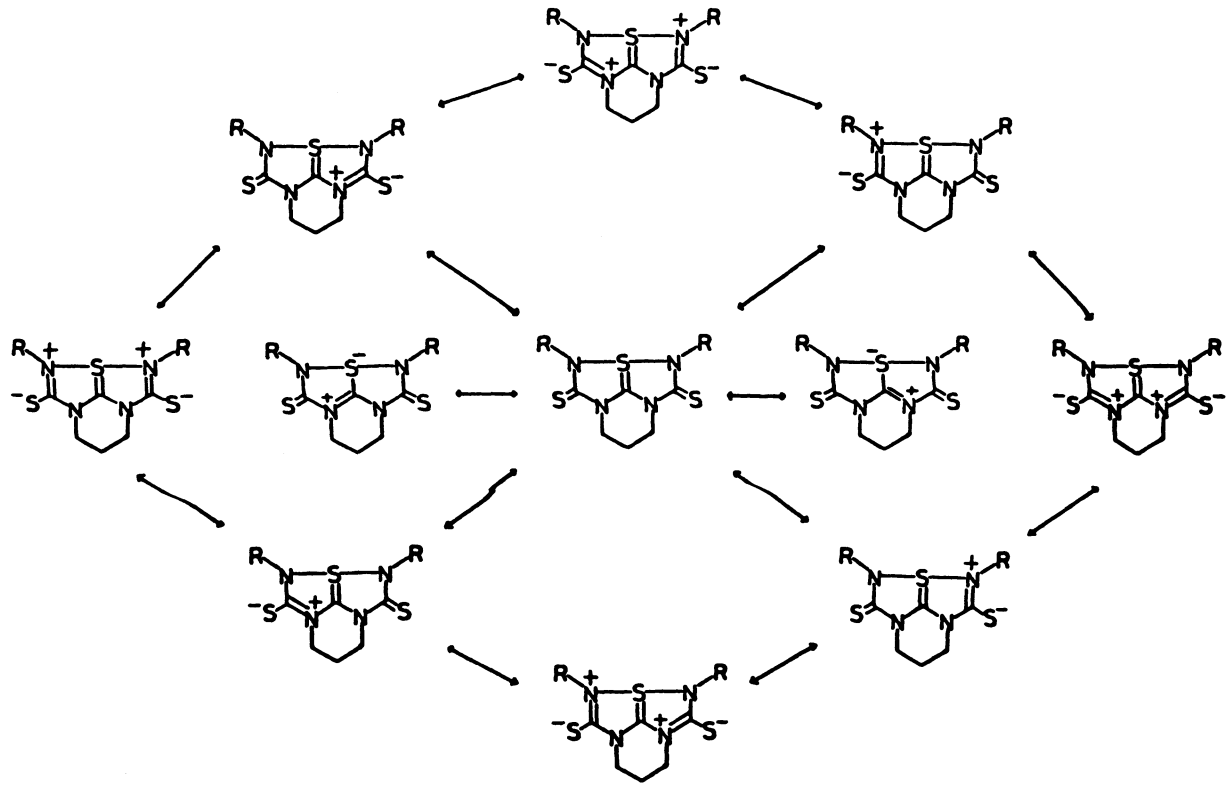
Fig. 3. Crystal packing diagram.

Table 4. Selected Bond Lengths and Angles of **5c** with Their Estimated Standard Deviations

Distance/Å		Angle/°	
S(1)–N(1)	1.927(4)	N(1)–S(1)–N(2)	165.5(2)
S(1)–N(2)	1.891(4)	N(1)–S(1)–C(2)	82.0(2)
S(1)–C(2)	1.705(4)	N(1)–C(1)–N(3)	108.7(4)
S(2)–C(1)	1.683(5)	N(1)–C(1)–S(2)	130.4(4)
S(3)–C(3)	1.674(5)	N(1)–C(7)–C(8)	112.5(4)
N(1)–C(1)	1.289(6)	N(2)–S(1)–C(2)	83.5(2)
N(1)–C(7)	1.461(6)	N(2)–C(3)–N(4)	108.5(4)
N(2)–C(3)	1.311(6)	N(2)–C(3)–S(3)	129.5(4)
N(2)–C(9)	1.438(7)	N(2)–C(9)–C(10)	112.1(5)
N(3)–C(1)	1.428(6)	N(3)–C(2)–N(4)	123.8(4)
N(3)–C(2)	1.327(6)	N(3)–C(4)–C(5)	108.9(4)
N(3)–C(4)	1.469(6)	N(4)–C(6)–C(5)	109.2(4)
N(4)–C(2)	1.339(6)	S(1)–N(1)–C(1)	116.0(3)
N(4)–C(3)	1.417(6)	S(1)–N(1)–C(7)	119.0(3)
N(4)–C(6)	1.469(6)	S(1)–N(2)–C(3)	115.7(3)
C(4)–C(5)	1.505(7)	S(1)–N(2)–C(9)	119.6(3)
C(5)–C(6)	1.519(7)	S(1)–C(2)–N(3)	119.0(3)
C(7)–C(8)	1.524(8)	S(1)–C(2)–N(4)	117.3(3)
C(9)–C(10)	1.494(8)	S(2)–C(1)–N(3)	120.9(3)
		S(3)–C(3)–N(4)	122.1(3)
		C(1)–N(1)–C(7)	125.1(4)
		C(1)–N(3)–C(2)	114.3(4)
		C(1)–N(3)–C(4)	125.5(4)
		C(2)–N(4)–C(3)	115.0(4)
		C(2)–N(3)–C(4)	120.2(4)
		C(2)–N(4)–C(6)	121.2(4)
		C(3)–N(2)–C(9)	124.5(4)
		C(3)–N(4)–C(6)	123.7(4)
		C(4)–C(5)–C(6)	110.7(4)

Table 5. Distances to the Plane from the Atoms in the Molecule

Atom	Distance/Å	Atom	Distance/Å
S(1)	0.002	S(3)	−0.015
N(1)	0.000	C(4)	−0.076
N(2)	−0.013	C(5)	0.629
N(3)	−0.006	C(6)	0.034
N(4)	0.010	C(7)	−0.027
C(1)	−0.002	C(8)	−1.413
C(2)	−0.003	C(9)	0.027
C(3)	−0.001	C(10)	1.422
S(2)	0.045		



Scheme 3.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and were uncorrected. Proton magnetic resonance (^{1}H NMR) spectra were obtained using a Hitachi Perkin-Elmer R-24 spectrometer (60 MHz), JEOL FX-90Q (90 MHz), and JEOL JNM-GX270 (270 MHz). ^{13}C NMR spectra were obtained using a JEOL FX-90Q and JEOL JNM-GX270. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. The IR and UV spectra were determined on a Hitachi 215 Grating infrared spectrometer and Hitachi 124 spectrometer, respectively. Mass spectra were obtained with a SHIMADZU-LKB 9000 instrument equipped with a solid injector; the ionizing voltage was 70 eV. Purifications of products were conducted by column chromatography on silica gel (Wakogel C-300) or by preparative TLC on silica gel (Merck Kieselgel 60 GF_{254}).

General Procedure for the Preparation of Symmetrical Tetraazapentalene Derivatives 5 and 6. To a cooled THF solution (0 °C, 25 ml) of cyclic thiourea **1** or **2** (2.0 mmol) was added a hexane solution of butyllithium (4.4 mmol) with stirring at 0 °C under argon, and the mixture was stirred for 1 h under the same conditions. To the resulting dianion **3** or **4** was added dropwise a THF solution (5 ml) of phenacyl chloride (2.0 mmol). The solution immediately became wine red, and the reaction mixture was refluxed for 1 h under argon. After cooling to room temperature, the 5 ml of solution of alkyl isothiocyanate (6.0 mmol) in THF was added, and the reaction mixture was stirred at room temperature for 20 h under argon. After THF was evaporated, the residue was poured into an aqueous ammonium chloride. The solution was extracted with chloroform, and the extract was washed with water, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on a silica-gel column or preparative TLC using dichloromethane as an eluent to give tetraazapentalene derivatives **5** or **6**. All tetraazapentalene derivatives were recrystallized from hexane–chloroform.

Spectroscopic data of 6,7-dihydro-2,3-dimethyl-5*H*-2a-thia(*2a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**5a**) and 6,7-dihydro-2,3-diethyl-5*H*-2a-thia-(2a-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**5c**) coincided with previously reported data.[2]

6,7-Dihydro-2,3-diallyl-5*H*-2a-thia(*2a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (5b). Mp 177—180 °C (decomp); IR (KBr) 2960, 1580, 1530, 1470, 1180, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.37 (m, 2H, $NCH_2\underline{CH_2}CH_2N$), 4.36 (t of d, 4H, J=1.5 and 6.0 Hz, $2\times CH_2$=CH$\underline{CH_2}$N), 4.37 (t, 4H, J=6.0 Hz, $NCH_2CH_2\underline{CH_2}N$), 5.20—5.28 (m, 4H, $2\times\underline{CH_2}$=CHCH$_2$N), and 5.88—6.02 (m, 2H, $2\times CH_2$=C$\underline{H}$-CH$_2$N); ^{13}C NMR ($CDCl_3$) δ=19.99, 44.84, 47.79, 118.10, 132.20, 156.66, and 169.57; UV (CH_3CN) 260 (log ε 4.52) nm; MS *m/z* (rel intensity) 213 (M^+-CH_2=CHCH$_2$NCS; 30), 99 (83), 72 (39), and 41 (100). Found: C, 46.02; H, 5.11; N, 17.91%. Calcd for $C_{12}H_{16}N_4S_3$: C, 46.12; H, 5.16; N, 17.93%.

5,6,7,8-Tetrahydro-2,3-dimethyl-2a-thia(*2a*-S^{IV})-2,3,4a,8a-tetraazacyclopent[*cd*]azulene-1,4(2*H*,3*H*)-dithione (6a). Mp 187—190 °C (decomp); IR (KBr) 2910, 1550, 1530, 1500, 1190, 1120, 1090 and 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.20 (m, 4H, $NCH_2\underline{CH_2}\underline{CH_2}CH_2N$), 3.15 (s, 6H, $2\times CH_3$), and 4.95 (m, 4H, $N\underline{CH_2}CH_2CH_2\underline{CH_2}N$); ^{13}C NMR ($CDCl_3$) δ=24.01, 31.49, 48.33, 161.49, and 170.78; UV (CH_3CN) 264 (log ε 4.56) nm; MS *m/z* (rel intensity) 201 (M^+-CH_3NCS; 91), 168 (32), 73 (100), 72 (81), and 69 (58). Found: C, 39.73; H, 5.19; N,

20.02%. Calcd for $C_9H_{14}N_4S_3$: C, 39.42; H, 5.15; N, 20.43%.

5,6,7,8-Tetrahydro-2,3-diallyl-2a-thia(2*a*-S^{IV})-2,3,4a,8a-tetraazacyclopent[*cd*]azulene-1,4(2*H*,3*H*)-dithione (6b). Mp 145—148 °C (decomp); IR (KBr) 2930, 2880, 1530, 1480, 1405, 1175, 1130, 1090, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.25 (m, 4H, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 4.33 (t of d, 4H, J=6.0 and 1.5 Hz, $2\times CH_2$=$CHC\underline{H}_2N$), 5.00 (m, 4H, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$), 5.20—5.27 (m, 4H, $2\times C\underline{H}_2$=$CHCH_2N$), and 5.87—6.02 (m, 2H, $2\times CH_2$=$C\underline{H}CH_2N$); ^{13}C NMR ($CDCl_3$) δ=23.96, 48.22, 48.38, 118.19, 132.01, 162.25, and 170.80; MS *m/z* (rel intensity) 227 (M^+-CH_2=$CHCH_2NCS$; 48), 194 (28), 114 (39), 99 (100), 72 (90), and 55 (50). Found: C, 47.30; H, 5.58; N, 17.01%. Calcd for $C_{13}H_{18}N_4S_3$: C, 47.82; H, 5.56; N, 17.16%.

5,6,7,8-Tetrahydro-2,3-diethyl-2a-thia(2*a*-S^{IV})-2,3,4a,8a-tetraazacyclopent[*cd*]azulene-1,4(2*H*,3*H*)-dithione (6c). Mp 159—162 °C (decomp); IR (KBr) 2960, 2920, 1550, 1530, 1430, 1190, 1080, and 980 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.32 (t, 6H, J=7.3 Hz, $2\times CH_2C\underline{H}_3$), 2.24 (m, 4H, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 3.75 (q, 4H, J=7.3 Hz, $2\times C\underline{H}_2CH_3$), and 5.00 (m, 4H, J=5.6 Hz, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$); ^{13}C NMR ($CDCl_3$) δ=13.68, 24.01, 40.30, 48.08, 161.72, and 169.81; UV (CH_3CN) 264 (log ε 4.54) nm; MS *m/z* (rel intensity) 215 ($M^+-CH_3CH_2$-NCS; 65), 182 (17), 114 (25), 87 (100), 72 (62), 59 (61), and 55 (54). Found: C, 43.73; H, 6.30; N, 18.20%. Calcd for $C_{11}H_{18}N_4S_3$: C, 43.68; H, 6.00; N, 18.52%.

General Procedure for the Preparation of Thiadiazolopyrimidine Derivatives 7. Method A (Thermolysis of **5**): Thermolysis of **5** (200 mg) using sublimation apparatus was carried out at 170 °C for 5 h under reduced pressure (2 mmHg). Then the sublimation products were collected with chloroform and chromatographed on a preparative TLC (dichloromethane:ethyl acetate=4:1 as an eluent) to give **7** as a colorless solid. Method B (Oxidation of **5** with $NaIO_4$): To a methanol solution (50 ml) of **5** (0.23 mmol) was added a sodium periodate (0.33 mmol) with stirring at room temperature under argon. After the stirring was continued for 5 h, methanol was removed in vacuo. To the residual mixture was added chloroform (50 ml), stirred for 1 min, and the resulting suspension was filtered. After the filtrate was condensed under reduced pressure, the residue was chromatographed on a preparative TLC (dichloromethane:ethyl acetate=4:1 as an eluent) to give **7** as a colorless solid.

6,7-Dihydro-2-methyl-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine-3(2*H*)-thione (7a). Mp 119—122 °C (decomp); IR(KBr) 2925, 2850, 1640, 1480, 1350, 1290, 1110, 945, and 750 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.90 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.35 (s, 3H, CH_3), 3.55 (t, 2H, J=6.0 Hz, C=NCH_2), and 3.90 (t, 2H, J=6.0 Hz, NCH_2); MS *m/z* (rel intensity) 187 (M^+; 100), 154 (23), 72 (33), 69 (38), and 41 (26).

Picrate of 7a. Mp 196—200°C (decomp); Found: C, 34.60; H, 2.85; N, 20.12%. Calcd for $C_{12}H_{12}N_6O_7S_2$: C, 34.61; H, 2.90; N, 20.18%.

6,7-Dihydro-2-allyl-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine-3(2*H*)-thione (7b). Mp 92—95 °C (decomp); IR (KBr) 2920, 2840, 1645, 1415, 1360, 1215, 1120, 855, and 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.10 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.65 (m, 2H, C=$NCH_2$), 4.00 (m, 2H, NCH_2), 4.55 (m, 2H, $NC\underline{H}_2CH$=CH_2), 5.20—5.65 (m, 2H, NCH_2CH=$C\underline{H}_2$), and 5.75—6.35 (m, 1H, $NCH_2C\underline{H}$=CH_2); MS *m/z* (rel intensity) 213 (M^+; 65), 180 (27), 128 (28), 100 (28), 99 (29), 72 (44), and 41 (100).

Picrate of 7b. Mp 171—174 °C (decomp); Found: C, 37.94; H, 3.02; N, 19.02%. Calcd for $C_{14}H_{14}N_6O_7S_2$: C, 38.01; H, 3.20; N, 18.99%.

6,7-Dihydro-2-ethyl-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine-3(2*H*)-thione (7c). Mp 86—88 °C (decomp); IR (KBr) 2920, 2850, 1640, 1480, 1295, 1215, 1120, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (t, 3H, J=7.0 Hz, $CH_2C\underline{H}_3$), 2.05 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.55 (t, 2H, J=6.0 Hz, C=NCH_2), 3.95 (q, 2H, J=7.0 Hz, $C\underline{H}_2CH_3$), and 4.35 (t, 2H, J=6.0 Hz, NCH_2); MS *m/z* (rel intensity) 201 (M^+; 100), 83 (43), 72 (50), 55 (39), and 41 (42).

Picrate of 7c. Mp 207—209 °C (decomp); Found: C, 36.24; H, 3.17; N, 19.16%. Calcd for $C_{13}H_{14}N_6O_7S_2$: C, 36.28; H, 3.28; N, 19.52%.

General Procedure for the Preparation of Unsymmetrical Tetraazapentalene Derivatives 8. A mixture of **7** (0.3 mmol) and isothiocyanate (0.45 mmol, 1.5 times molar quantity of **7**) in chloroform (30 ml) was refluxed for 3 h. After the solvent was removed, the residue was chromatographed on a preparative TLC (dichloromethane as an eluent) to give **8**. Recrystallization from hexane–chloroform gave a pure sample as a colorless solid.

6,7-Dihydro-2-methyl-3-ethyl-5*H*-2a-thia(2*a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (8d). Mp 200—202 °C (decomp); IR (KBr) 2960, 2920, 1575, 1540, 1495, 1310, 1240, 1185, and 1120 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.32 (t, 3H, J=7.2 Hz, $CH_2C\underline{H}_3$), 2.36 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.22 (s, 3H, CH_3), 3.78 (q, 2H, J=7.2 Hz, $C\underline{H}_2CH_3$), and 4.41 (t, 4H, J=6.0 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$); ^{13}C NMR($CDCl_3$) δ=13.86, 20.04, 31.15, 39.89, 44.67, 44.85, 156.00, 168.72, and 169.52; UV (CH_3CN) 259 (log ε 4.53) nm; MS *m/z* (rel intensity) 201 (M^+-CH_3NCS; 17), 187 ($M^+-CH_3CH_2NCS$; 25), 116 (22), 87 (100), 73 (89), 72 (45), 69 (22), and 59 (43). Found: C, 39.59; H, 5.31; N, 19.93%. Calcd for $C_9H_{14}N_4S_3$: C, 39.42; H, 5.15; N, 20.43%.

6,7-Dihydro-2-methyl-3-phenyl-5*H*-2a-thia(2*a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (8e). Mp 179—182 °C (decomp); IR (KBr) 2920, 1570, 1530, 1450, 1320, 1245, 1165, 1130, 955, and 785 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.35 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.20 (s, 3H, CH_3), 4.40 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$), and 7.30 (s, 5H, aromatic); UV (CH_3CN) 257 (log ε 4.49) nm; MS *m/z* (rel intensity) 249 (M^+-CH_3NCS; 2), 187 ($M^+-C_6H_5NCS$; 58), 154 (16), 135 (100), 77 (62), 72 (26), and 69 (29). Found: C, 48.36; H, 4.45; N, 17.37%. Calcd for $C_{13}H_{14}N_4S_3$: C, 48.42; H, 4.38; N, 17.37%.

6,7-Dihydro-2-methyl-3-(*p*-chlorophenyl)-5*H*-2a-thia(2*a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (8f). Mp 188—191 °C(decomp); IR(KBr) 3040, 1560, 1515, 1495, 1305, 1240, 1120, 835, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.40 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.25 (s, 3H, CH_3), 4.40 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$), and 7.30 (s, 4H, aromatic); ^{13}C NMR($CDCl_3$) δ=20.06, 31.44, 45.06, 45.23, 126.55, 129.44, 132.48, 137.40, 156.88, 169.27, and 170.23; UV(CH_3CN) 268 (log ε 4.49) nm; MS *m/z* (rel intensity) 283 (M^+-CH_3NCS; 1), 187 (M^+-p-ClC_6H_4NCS; 41), 171 (36), 169 (100), 154 (10), 113 (13), 111 (36), 75 (24), 72 (19), and 69 (19). Found: C, 43.45; H, 3.69; N, 15.50%. Calcd for $C_{13}H_{13}N_4S_3Cl$: C, 43.75; H, 3.67; N, 15.70%.

6,7-Dihydro-2-methyl-3-allyl-5*H*-2a-thia(2*a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (8g). Mp

185—188 °C(decomp); IR(KBr) 2930, 1570, 1530, 1485, 1305, 1235, 1180, 1115, 935, and 840 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.37 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.22 (s, 3H, CH_3), 4.34—4.40 (m, 2H, $NC\underline{H}_2CH=CH_2$), 4.42 (t, 4H, J=6.0 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 5.20—5.28 (m, 2H, $NCH_2CH=C\underline{H}_2$), and 5.88—6.03 (m, 1H, $NCH_2C\underline{H}=CH_2$); MS m/z (rel intensity) 213 (M^+-CH_3NCS; 23), 187 ($M^+-CH_2=CHCH_2NCS$; 54), 99 (72), 73 (51), 72 (72), and 41 (100). Found: C, 42.08; H, 4.87; N, 19.12%. Calcd for $C_{10}H_{14}N_4S_3$: C, 41.89; H, 4.92; N, 19.54%.

6,7-Dihydro-2-ethyl-3-allyl-5*H*-2a-thia(2a-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (8h). Mp 186—189 °C (decomp); IR (KBr) 2960, 2900, 1575, 1535, 1485, 1305, 1235, 1180, and 1120 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.30 (t, 3H, J=7.0 Hz, $CH_2C\underline{H}_3$), 2.35 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.75 (q, 2H, J=7.0 Hz, $C\underline{H}_2CH_3$), 4.20—4.50 (m, 6H, $NC\underline{H}_2CH=CH_2$ and $NC\underline{H}_2CH_2C\underline{H}_2N$), 5.00—5.35 (m, 2H, $NCH_2CH=C\underline{H}_2$), and 5.70—6.20 (m, 1H, $NCH_2C\underline{H}=CH_2$); MS m/z (rel intensity) 213 ($M^+-CH_3CH_2NCS$; 23), 201 ($M^+-CH_2=CHCH_2NCS$; 81), 99 (55), 87 (90), 72 (85), 59 (61), and 41 (100). Found: C, 43.40; H, 5.49; N, 18.65%. Calcd for $C_{11}H_{16}N_4S_3$: C, 43.97; H, 5.37; N, 18.64%.

6,7-Dihydro-2-allyl-3-(*p*-chlorophenyl)-5*H*-2a-thia(2a-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (8i). Mp 140—142 °C (decomp); IR (KBr) 1575, 1520, 1500, 1455, 1315, 1240, 1220, 1150, 1080, 955, 915, and 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.35 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 4.20—4.55 (m, 6H, $NC\underline{H}_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH=CH_2$), 5.00—5.35 (m, 2H, $NCH_2CH=C\underline{H}_2$), 5.50—6.00 (m, 1H, $NCH_2C\underline{H}=CH_2$), and 7.20 (s, 4H, aromatic); MS m/z (rel intensity) 283 ($M^+-CH_2=CHCH_2NCS$; 2), 213 (M^+-p-ClC_6H_4NCS; 29), 171 (43), 169 (100), 111 (41), 99 (21), 75 (29), 72 (23), and 41 (48). Found: C, 46.94; H, 3.85; N, 14.42%. Calcd for $C_{15}H_{15}N_4S_3Cl$: C, 47.05; H, 3.95; N, 14.63%.

X-Ray Crystallographic Analysis of 5c.[7] A colorless crystal of **5c** was grown from hexane–chloroform solution. The crystal shape was a hexagonal prism. A single crystal of dimensions 0.52×0.24×0.17 mm was selected for X-ray investigations. Data were collected on a Rigaku AFC-5 diffractometer using Mo $K\alpha$ radiation. Reflections in the range $2\theta \leq 55°$ were measured by the ω/θ–2θ scan technique with a scan width of $1.4°+0.5°\tan\theta$. The structure was solved by the direct method with MULTAN 78[8] and refined by block-diagonal least-squares to final R value of 0.043 for 1315 absorption corrected[9] independent reflection [$|F_o|>3\sigma(F_o)$]. The weighting scheme $w=[\sigma^2_{count}+(0.03|F_o|)^2]^{-1}$ was employed. Crystal data for **5c** are as follows: $C_{10}H_{16}N_4S_3$, M=288.433, monoclinic, space group $P2_1$, a=13.060(5) Å, b=9.988(3) Å, c=5.211(2) Å, β=98.31(3)°, U=672.6(4) Å^3, Z=2, D_c=1.42 g cm^{-3}, $F(000)$=304, μ(Mo $K\alpha$)=5.19 cm^{-1}.

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