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12π-Tetraazapentalenes, 2,3-disubstituted 6,7-dihydro-5*H*-2a-thia(2a-*S*<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithiones, **1** and **7**, reacted with excess alkyl or aryl isothiocyanates and isocyanates to afford mono- and di-alkyl or aryl substituted tetraazapentalene derivatives which have the thiocarbonyl and carbonyl groups.

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In recent years, much attention has been paid on hyper-valent heterocyclic π-electron systems, especially the 10π-systems involving the S-*S*<sup>IV</sup>-S, S-*S*<sup>IV</sup>-O, and N-*S*<sup>IV</sup>-N bonds [1a-f]. We have recently synthesized the 12π-tetraazapentalene derivative, 2,3-dimethyl-6,7-dihydro-5*H*-2a-thia(2a-*S*<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**1**), by a convenient one-pot reaction using the lithium thioureide/phenacyl chloride/methyl isothiocyanate system [2], and reported that the reactivity of **1** is different from that of the 10π-systems [3a-d]. In the course of further studies on the reactivity of **1**, we have found that **1** reacts with excess *p*-chlorophenyl isothiocyanate and methyl isocyanate to give the tetraazapentalene derivatives, **5** and **12**, respectively, which can not be synthesized from lithium thioureide by the one-pot reaction [4]. In this

paper, we report the details of the reactions of the tetraazapentalenes, **1** and **7**, with various isothiocyanates and isocyanates and the spectral characterization of the novel tetraazapentalenes.

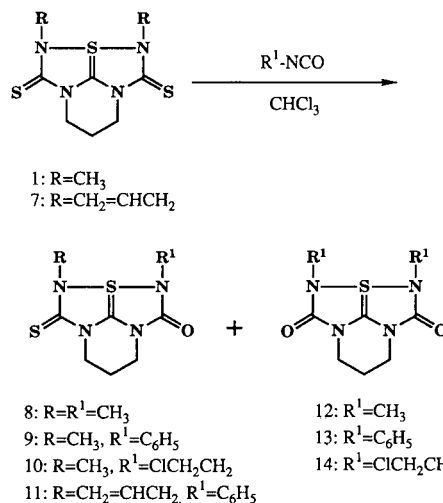
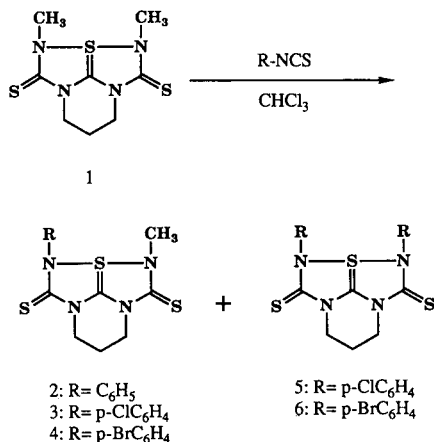
The reactions of **1** with 5 molar equivalents of various alkyl and aryl isothiocyanates (EtNCS, PhNCS, *p*-ClPhNCS, and *p*-BrPhNCS) in chloroform were carried out under reflux. After chloroform was removed, the chromatography of the residue on a preparative tlc gave the mono- and di-substituted tetraazapentalenes, **2-6**. Table 1 shows the yields of the products and the recovered **1**. The structure of products was determined by ir, <sup>1</sup>H nmr, <sup>13</sup>C nmr, and mass spectra, and elemental analysis.

As shown in Table 1, the reaction of **1** with ethyl isothiocyanate did not give any substituted tetraazapentalene. On the other hand, the reaction of **1** with phenyl isothiocyanate gave only the mono-substituted tetraazapentalene **2** in 43% yield. When *p*-chloro- and *p*-bromophenyl isothiocyanates were used, the di-substituted tetraazapentalenes, **5** and **6**, were obtained in small amounts together with the mono-substituted tetraazapentalenes, **3** and **4**, respectively. In the reaction of **1** with *p*-chlorophenyl isothiocyanate, the elongation of the reaction time resulted in the increase

Table 1  
Reaction of **1** with Various Isothiocyanates [a]

Isothiocyanate	Time (hour)	Product (yield, %) [b]	Recovered <b>1</b> (%)
CH <sub>3</sub> CH <sub>2</sub> NCS	48	None	96
C <sub>6</sub> H <sub>5</sub> NCS	20	<b>2</b> (43)	27
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NCS	20	<b>3</b> (40); <b>5</b> (7)	40
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NCS	112	<b>3</b> (35); <b>5</b> (12)	29
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> NCS	20	<b>4</b> (37); <b>6</b> (9)	20

[a] All reactions were carried out under reflux in chloroform. [b] Isolated yields are based on **1**.



of the yield of the di-substituted product **5**. This method is very useful and convenient for the synthesis of tetraazapentalenes having one or two aryl groups.

Next, we examined the reaction of the tetraazapentalene derivatives, **1** and **7**, with various isocyanates. When the reaction of **1** or **7** with 10 molar equivalents of various isocyanates ( $R^1\text{-NCO}$ ) in chloroform was carried out under reflux for 6 hours, the mono-substituted tetraazapentalenes, **8-11**, with a carbonyl group and the di-substituted tetraazapentalenes, **12-14**, with two carbonyl groups were obtained in relatively good yields.

Table 2 shows the yields of the products, **8-14**. The structure of all products was determined by ir,  $^1\text{H}$  nmr, and mass spectra, and elemental analysis. The compound **12** was isolated as a monohydrate (see Experimental).

Table 2  
Reactions of **1** and **7** with Various Isocyanates [a]

Tetraazapentalene	Isocyanate	Product (yield, %) [b]
<b>1</b>	$\text{CH}_3\text{NCO}$	<b>8</b> (32), <b>12</b> (26)
<b>1</b>	$\text{C}_6\text{H}_5\text{NCO}$	<b>9</b> (53), <b>13</b> (30)
<b>1</b>	$\text{ClCH}_2\text{CH}_2\text{NCO}$	<b>10</b> (32), <b>14</b> (21)
<b>7</b>	$\text{CH}_3\text{NCO}$	<b>12</b> (78)
<b>7</b>	$\text{C}_6\text{H}_5\text{NCO}$	<b>11</b> (55), <b>13</b> (35)
<b>7</b>	$\text{ClCH}_2\text{CH}_2\text{NCO}$	<b>14</b> (78)

[a] Reaction of **1** with various isocyanates in chloroform was carried out under reflux for 6 hours. Molar ratio of **1** to isocyanate = 1:10. [b] Isolated yields are based on **1**.

As shown in Table 2, the yields of **8-14** depended on the kinds of the substituents of isocyanates and tetraazapentalenes **1** and **7**. Generally, the yields of the di-substituted tetraazapentalenes, **12-14**, from **7** were better than those from **1**. Furthermore, it was found that the substitution reactions of **1** and **7** with isocyanates proceed more smoothly than those with isothiocyanates. As the di-substituted

tetraazapentalenes, **12-14**, are not prepared by the one-pot reaction using the lithium thioureide/phenacyl chloride/isocyanate system, the substitution reactions shown here are very useful for the synthesis of the tetraazapentalene derivatives with the carbonyl groups.

The reaction of **1** with  $R\text{-NCX}$  ( $X = \text{S}$  or  $\text{O}$ ) is considered to proceed by the process of path A rather than path B, as shown in Scheme 1, because (a) the heating of **1** at  $170^\circ$  under reduced pressure (2 mm Hg) is required for the removal of methyl isothiocyanate from **1** to give **15** [5], and (b) the  $^1\text{H}$  nmr spectrum of **1** in benzene- $d_6$  at  $61^\circ$  is the same as that at room temperature. That is, the reaction would proceed by the nucleophilic attack of the nitrogen atom at the 4a-position of **1** on  $R\text{-NCX}$ , followed by the cleavage of the  $S^{\text{IV}}\text{-N}$  bond to form the mono-substituted tetraazapentalenes. Further substitution reaction by  $R\text{-NCX}$  results in the formation of the di-substituted tetraazapentalenes.

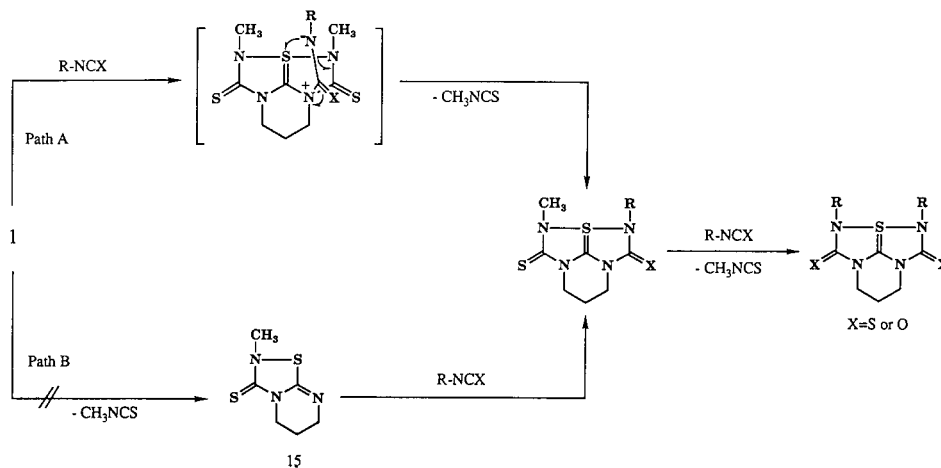
## EXPERIMENTAL

Melting points were determined on a Yanagimoto MP-S3 melting point apparatus and were uncorrected. The  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were obtained using a JEOL JNM-GX270 spectrometer (270 MHz). Chemical shifts are reported in ppm from TMS as an internal standard and are given in  $\delta$  units. The ir spectra were determined on a Hitachi 215 Grating infrared spectrometer. 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 a preparative tlc on silica-gel (Merck Kieselgel 60 GF<sub>254</sub>).

Typical Procedure for the Reaction of **1** with Isothiocyanate.

To a solution of **1** (52 mg, 0.20 mmole) in chloroform (25 ml) was added *p*-chlorophenyl isothiocyanate (169 mg, 1.0 mmole) with stirring, and the reaction mixture was refluxed for 20 hours. After chloroform was evaporated under reduced pressure, the residue was chromatographed on a preparative tlc (silica-gel, dichloromethane as an eluent) to give **3** (Rf 0.5, 28 mg, 40%), **5** (Rf

Scheme 1



0.6, 6 mg, 7%), and the recovered **1** (Rf 0.3, 21 mg, 40%). Recrystallization from hexane-chloroform or methanol gave pure samples.

2-Methyl-3-phenyl-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**2**).

This compound was obtained from the reaction of **1** with phenyl isothiocyanate as a colorless solid, mp 179-182° dec. Spectroscopic data of **2** coincided with previously reported data [2].

2-Methyl-3-(*p*-chlorophenyl)-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**3**).

This compound was obtained from the reaction of **1** with *p*-chlorophenyl isothiocyanate as a colorless solid, mp 188-191° dec. Spectroscopic data of **3** coincided with previously reported data [2].

2-Methyl-3-(*p*-bromophenyl)-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**4**).

This compound was obtained from the reaction of **1** with *p*-bromophenyl isothiocyanate as a colorless solid, mp 190-193° dec; ir (potassium bromide): 3050, 2950, 1575, 1530, 1500, 1320, 1245, 1130, and 1070 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.43 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.26 (s, 3H, CH<sub>3</sub>), 4.42 (t, 2H, J = 5.5 Hz, NCH<sub>2</sub>), 4.53 (t, 2H, J = 5.5 Hz, NCH<sub>2</sub>), and 7.26-7.60 (AA'XX' type, 4H, aromatic); <sup>13</sup>C nmr (deuteriochloroform): δ 20.12, 31.49, 45.09, 45.27, 120.47, 126.93, 132.44, 137.95, 157.71, 170.84, and 172.60; ms: m/z (relative intensity) 216 (100), 214 (*p*-BrC<sub>6</sub>H<sub>4</sub>NCS; 98), 187 (M<sup>+</sup> -*p*-BrC<sub>6</sub>H<sub>4</sub>NCS, 47), 157 (15), 155 (17), 134 (31), 76 (13), 75 (21), 74 (14), 73 (20), 72 (22), and 69 (19).

Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>4</sub>S<sub>2</sub>Br: C, 38.90; H, 3.26; N, 13.96. Found: C, 38.71; H, 3.25; N, 14.10.

2,3-Bis(*p*-chlorophenyl)-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**5**).

This compound was obtained from the reaction of **1** with *p*-chlorophenyl isothiocyanate as a colorless solid, mp 173-176° dec; ir (potassium bromide): 2910, 1565, 1505, 1440, 1315, 1255, 1220, 1150, 1085, and 835 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.45 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.50 (t, 4H, J = 6.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), and 7.30 (s, 8H, aromatic); ms: m/z (relative intensity): 285 (2), 283 (M<sup>+</sup> -*p*-ClC<sub>6</sub>H<sub>4</sub>NCS, 5), 219 (4), 171 (37), 169 (100), 137 (11), 113 (15), 111 (38), and 75 (19).

Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub>: C, 47.68; H, 3.11; N, 12.36. Found: C, 47.69; H, 3.48; N, 12.24.

2,3-Bis(*p*-bromophenyl)-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**6**).

This compound was obtained from the reaction of **1** with *p*-bromophenyl isothiocyanate as a colorless solid, mp 192-195° dec; ir (potassium bromide): 2970, 1575, 1515, 1490, 1430, 1315, 1255, 1155, 1095, 1005, 835, and 740 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.49 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.53 (t, 4H, J = 6.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), and 7.23-7.59 (AA'XX' type, 8H, aromatic); ms: m/z (relative intensity) 329 (10), 327 (M<sup>+</sup> -*p*-BrC<sub>6</sub>H<sub>4</sub>NCS; 9), 265 (7), 263 (7), 216 (100), 214 (94), 157 (17), 155 (16), 134 (28), 116 (11), 90 (11), 86 (14), and 85 (19).

Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>S<sub>2</sub>Br<sub>2</sub>: C, 39.86; H, 2.60; N, 10.33. Found: C, 39.98; H, 3.00; N, 10.16.

Typical Procedure for the Reactions of **1** and **7** with Isocyanate.

To a solution of **1** (83 mg, 0.32 mmole) in chloroform (30 ml) was added methyl isocyanate (182 mg, 3.2 mmoles) with stirring at room temperature. After the reaction mixture was refluxed for 6 hours, chloroform was evaporated under reduced pressure. The residue was chromatographed on a preparative tlc (silica-gel, ethyl acetate as an eluent) to give **8** (Rf 0.4, 25 mg, 32%) and **12** (Rf 0.1, 20 mg, 26%) as colorless solids. Recrystallization from hexane-chloroform or methanol gave pure samples.

2,3-Dimethyl-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H)-one-4(3H)-thione (**8**).

This compound was obtained from the reaction of **1** with methyl isocyanate as a colorless solid, mp 183-185°; ir (potassium bromide): 2925, 1695, 1595, 1535, 1400, 1310, 1240, 1185, 1050, 990, and 745 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.29 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.95 (s, 3H, NCH<sub>3</sub>), 3.19 (s, 3H, NCH<sub>3</sub>), 3.99 (t, 2H, J = 5.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), and 4.38 (t, 2H, J = 5.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C nmr (deuteriochloroform): δ 19.58, 26.25, 30.85, 40.39, 44.13, 150.09, 157.51, and 170.30; ms: m/z (relative intensity): 187 (M<sup>+</sup> -CH<sub>3</sub>NCO, 100), 171 (M<sup>+</sup> -CH<sub>3</sub>NCS, 19), 73 (62), 69 (51), and 57 (71).

Anal. Calcd. for C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>OS<sub>2</sub>: C, 39.32; H, 4.95; N, 22.93. Found: C, 39.10; H, 4.65; N, 22.64.

2-Phenyl-3-methyl-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H)-one-4(3H)-thione (**9**).

This compound was obtained from the reaction of **1** with phenyl isocyanate as a colorless solid, mp 161-162.5°; ir (potassium bromide): 2950, 1700, 1600, 1535, 1435, 1400, 1360, 1250, 1190, 1120, 1050, and 760 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.24 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.20 (s, 3H, NCH<sub>3</sub>), 3.98 (t, 2H, J = 5.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.27 (t, 2H, J = 5.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), and 7.12-7.41 (m, 5H, aromatic); <sup>13</sup>C nmr (deuteriochloroform): δ 19.67, 31.31, 40.59, 44.55, 123.16, 125.04, 129.25, 138.47, 148.17, 158.88, and 171.21; ms: m/z (relative intensity) 187 (M<sup>+</sup> -C<sub>6</sub>H<sub>5</sub>NCO, 25), 119 (100), 91 (38), 73 (20), 64 (24).

Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>OS<sub>2</sub>: C, 50.96; H, 4.61; N, 18.29. Found: C, 50.61; H, 4.38; N, 18.45.

2-(2-Chloroethyl)-3-methyl-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H)-one-4(3H)-thione (**10**).

This compound was obtained from the reaction of **1** with 2-chloroethyl isocyanate as a colorless solid, mp 153-155°; ir (potassium bromide): 1690, 1590, 1530, 1425, 1240, and 1050 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.31 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.21 (s, 3H, NCH<sub>3</sub>), 3.68 (s, 4H, NCH<sub>2</sub>CH<sub>2</sub>Cl), 4.00 (t, 2H, J = 5.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), and 4.37 (t, 2H, J = 5.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C nmr (deuteriochloroform): δ 19.62, 31.07, 40.47, 42.67, 42.81, 44.33, 150.65, 158.18, and 170.65; ms: m/z (relative intensity) 187 (M<sup>+</sup> -ClCH<sub>2</sub>CH<sub>2</sub>NCO, 71), 73 (19), 69 (43), 56 (100), 41 (30).

Anal. Calcd. for C<sub>9</sub>H<sub>13</sub>N<sub>4</sub>OS<sub>2</sub>Cl: C, 36.92; H, 4.48; N, 19.13. Found: C, 36.68; H, 4.43; N, 18.82.

2-Phenyl-3-allyl-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H)-one-4(3H)-thione (**11**).

This compound was obtained from the reaction of **7** with phenyl isocyanate as a colorless solid, mp 67-69°; ir (potassium

bromide): 1690, 1590, 1350, 1240, 1160, 1120, and 750  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.35 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 4.08 (t, 2H,  $J = 5.8$  Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 4.36-4.40 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$  and  $\text{NCH}_2\text{CH}=\text{CH}_2$ ), 5.23-5.30 (m, 2H,  $\text{NCH}_2\text{CH}=\text{CH}_2$ ), 5.94-6.02 (m, 1H,  $\text{NCH}_2\text{CH}=\text{CH}_2$ ), 7.14-7.45 (m, 5H, aromatic); ms:  $m/z$  (relative intensity) 213 ( $\text{M}^+ \cdot \text{C}_6\text{H}_5\text{NCO}$ , 22), 119 (100), 91 (40), 64 (23), 41 (39).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ : C, 54.19; H, 4.85; N, 16.85. Found: C, 53.90; H, 4.60; N, 16.88.

2,3-Dimethyl-6,7-dihydro-5*H*-2a-thia(2a- $S^{IV}$ )-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dione Monohydrate (**12**).

This compound was obtained from the reactions of **1** and **7** with methyl isocyanate as a colorless solid, mp 162.5-165 $^\circ$ ; ir (potassium bromide): 3510, 2920, 1675, 1615, 1410, 1340, 1055, 1000, 925, and 740  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.23 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 2.90 (s, 6H, 2 x  $\text{NCH}_3$ ), and 3.94 (t, 4H,  $J = 5.5$  Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  19.34, 26.19, 39.94, 151.42, and 159.34; ms:  $m/z$  (relative intensity) 171 ( $\text{M}^+ \cdot \text{CH}_3\text{NCO} \cdot \text{H}_2\text{O}$ , 100), 114 (29), 75 (40), 61 (67), and 57 (93).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_3\text{S}$ : C, 39.01; H, 5.73; N, 22.75. Found: C, 38.96; H, 5.77; N, 22.57.

2,3-Diphenyl-6,7-dihydro-5*H*-2a-thia(2a- $S^{IV}$ )-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dione (**13**).

This compound was obtained from the reactions of **1** and **7** with phenyl isocyanate as a colorless solid, mp 211-212 $^\circ$ ; ir (potassium bromide): 1700, 1680, 1610, 1500, 1345, 970, 765, and 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.35 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 4.07 (t, 4H,  $J = 5.8$  Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), and 7.15-7.45 (m, 10H, aromatic);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  19.34, 40.36, 123.04, 125.12, 129.32, 138.26, 149.22, and 160.74; ms:  $m/z$  (relative intensity) 233 ( $\text{M}^+ \cdot \text{C}_6\text{H}_5\text{NCO}$ , 3), 119 (100), 92 (56), 64 (33), 39 (11).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ : C, 61.35; H, 4.58; N, 15.90. Found: C, 61.41; H, 4.31; N, 16.26.

2,3-Bis(2-chloroethyl)-6,7-dihydro-5*H*-2a-thia(2a- $S^{IV}$ )-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dione (**14**).

This compound was obtained from the reactions of **1** and **7** with 2-chloroethyl isocyanate as a colorless solid, mp 211-212 $^\circ$ ; ir (potassium bromide): 1685, 1595, 1330, 1300, and 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.27 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 3.67 (s, 8H, 2 x  $\text{NCH}_2\text{CH}_2\text{Cl}$ ), and 3.97 (t, 4H,  $J = 6.1$  Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  19.20, 40.05, 42.73, 42.98, 151.43, and 160.14; ms:  $m/z$  (relative intensity) 219 ( $\text{M}^+ \cdot \text{ClCH}_2\text{CH}_2\text{NCO}$ , 38), 170 (65), 105 (11), 56 (100), 42 (16).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2\text{SCl}_2$ : C, 36.93; H, 4.34; N, 17.23. Found: C, 36.62; H, 4.20; N, 17.00.

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