Synthesis and Reactivities of 10-*S*-3 Trithiadiazapentalene Derivatives

Noboru Matsumura*, Motoyuki Kusamiya, and Hiroo Inoue

Department of Applied Chemistry, College of Engineering, University Of Osaka Prefecture,
Sakai, Osaka 593, Japan

Masanori Yasui and Fujiko Iwasaki

Department of Applied Physics and Chemistry, The University of Electro-Communications,
Chofu-shi, Tokyo 182, Japan

Received February 21, 1995

1,3-Bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinethiones **3a-f** reacted with bromine to give trithiadiazapentalene derivatives **5a-f**, bearing the exocyclic C-N double bonds, in moderate yields. The molecular structure of **5b** was elucidated by the X-ray crystallographic analysis. The treatment of **5b-f** with hydrochloric acid gave the ring-opening products, 1,3-bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinones **9b-f**, accompanied by the production of elemental sulfur. Reduction of **5b**, **5d**, and **5e** with sodium borohydride gave the ring-opening compounds, 1,3-bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidines **13b**, **13d**, and **13e** respectively.

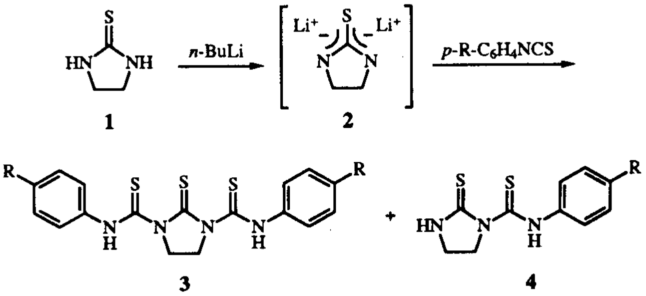
J. Heterocyclic Chem., 32, 1269 (1995).

Recently, the chemistry of 1,6,6a-trithia(6a-S^{IV})pentalenes has attracted considerable attention because of their unusual electronic structure, and many 6a-thia(S^{IV})pentalene derivatives containing 10 π electrons in the framework have been synthesized [1]. However, little is known about the chemistry of trithiadiazapentalene derivatives with the exocyclic C-N double bonds [2]. In the course of our study [3] on the chemistry of 10-*S*-3 sulfuranes, we have found that (1) the oxidation of 1,3-bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinethiones **3a-f** with bromine gives trithiadiazapentalene derivatives **5a-f**, (2) the treatment of **5b-f** with hydrochloric acid gives the ring-opening products, 1,3-bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinones **9b-f** and sulfur, and (3) the reduction of **5b**, **5d**, and **5e** with sodium borohydride gives the ring-opening products, 1,3-bis(*p*-substituted-phenylthiocarbamoyl)imidazolidines **13b**, **13d**, and **13e**, respectively by the reductive-elimination of the C=S^{IV} moiety. In this paper, the details of these results are described.

Results and Discussion.

Synthesis of 1,3-Bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinethiones 3a-f.

Treatment of ethylene thiourea (**1**) with 2 equivalents of *n*-butyllithium in THF at 0° under argon gave dianion **2**. When this dianion was allowed to react with 3 equivalents of *p*-substituted-phenylisothiocyanates under the same conditions, 1,3-bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinethiones **3a-f** and 1-(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinethiones **4a-f** were obtained as yellowish solids in moderate yields (Table 1). The structures of **3a-f** and **4a-f** were determined by their ir, ^{1}H nmr, and mass spectra, and elemental analyses.



a: R = NO$_2$ **b**: R = Cl **c**: R = Br **d**: R = H **e**: R = CH$_3$ **f**: R = CH$_3$O

Table 1

Reaction of **2** with *p*-Substituted-phenylisothiocyanates [a]

Entry	R in *p*-RC$_6$H$_4$NCS	Product (Yields, %) [b]	
1	NO$_2$	**3a** (35)	**4a** (30)
2	Cl	**3b** (31)	**4b** (64)
3	Br	**3c** (58)	**4c** (31)
4	H	**3d** (46)	**4d** (41)
5	CH$_3$	**3e** (32)	**4e** (67)
6	CH$_3$O	**3f** (21)	**4f** (67)

[a] Reactions were carried out in tetrahydrofuran at 0° for 3 hours. [b] Isolated yields are based on **1**.

Synthesis and Structural Analysis of 10-*S*-3 Trithiadiazapentalene Derivatives 5a-f.

The reactions of **3a-f** with 1 equivalent of bromine in dichloromethane under argon at room temperature, followed by treatment with an aqueous sodium bicarbonate solution, gave 2,3,4,5-tetrahydro-2,5-bis(*p*-substituted-phenylimino)-3,4-ethano-1,6,6aλ^4-trithia-3,4-diazapentalenes **5a-f** as yellow solids. The yields and the analytical and spectral data of the products are given in Tables 2, 3

Table 2

Reaction of **3a-f** with Bromine [a]

Entry	2-Imidazolidinethione Derivative	Product	Yield (%) [b]
1	**3a** (R = NO_2)	**5a**	48
2	**3b** (R = Cl)	**5b**	70
3	**3c** (R = Br)	**5c**	61
4	**3d** (R = H)	**5d**	62
5	**3e** (R = CH_3)	**5e**	68
6	**3f** (R = CH_3O)	**5f**	81

[a] The reactions were carried out in dichloromethane at room temperature for 10 minutes. [b] Isolated yields.

and 4, respectively. These compounds were stable under exposure to the atmosphere.

X-ray Diffraction of **5b**.

Figure 1 shows an ORTEP II [4] drawing of **5b**. Figure 2 shows the molecular structure of **5b** viewed along the S(6a)-C(3a) bond.

The X-ray diffraction study indicates that **5b** has a trithiadiazapentalene skeleton with exocyclic C-N double bonds. The S(1)-S(6a) [2.488(3) Å] and S(6)-S(6a) [2.314(4) Å] bond lengths differ from each other, showing that **5b** has an unsymmetrical structure. The configuration

Table 3

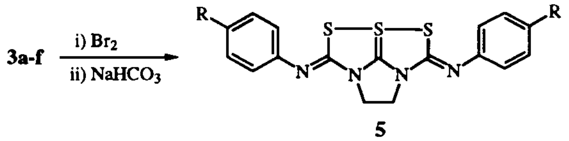
Melting Points and Analytical Data of Trithiadiazapentalene Derivatives **5a-f**

Compound	R	Mp, °C	Molecular Formula	Analysis % Calcd./Found C	H	N
5a	NO_2	206.5-207.5	$C_{17}H_{12}N_6O_4S_3$	44.33 44.22	2.63 2.46	18.25 18.10
5b	Cl	186.5-187.5	$C_{17}H_{12}N_4S_3Cl_2$	46.46 46.55	2.75 2.51	12.75 12.82
5c	Br	206-207	$C_{17}H_{12}N_4S_3Br_2$	38.65 38.82	2.29 2.17	10.61 10.61
5d	H	162-164	$C_{17}H_{14}N_4S_3$	55.10 54.92	3.81 3.51	15.12 15.15
5e	CH_3	161-162.5	$C_{19}H_{18}N_4S_3$	57.25 57.05	4.55 4.36	14.06 14.05
5f	CH_3O	155.5-156.5	$C_{19}H_{18}N_4O_2S_3$	52.99 52.85	4.21 3.98	13.01 13.28

Table 4

Spectral Data of Trithiadiazapentalene Dervatives

Compound	R	IR (cm^{-1}) (Potassium Bromide)	^{1}H NMR (δ, ppm) (Solvent)	FAB MS $(M+H)^+$, m/z	UV λ max (ε) (DMSO)
5a	NO_2	1581, 1509, 1450, 1329, 1288, 1168, 1105, 923, 850, 759, 697	(DMSO-d_6) 4.49 (s, 4H, N-CH_2CH_2N), 7.18-8.25 (AA'XX' type, 8H, 2x $C_6H_4NO_2$)	461	357 (38400)
5b	Cl	1597, 1567, 1522, 1494 1481, 1448, 1357, 1284 1184, 1089, 1006, 920, 888, 839, 617, 537, 520	($CDCl_3$) 4.61 (s, 4H, NCH_2-CH_2N), 6.98-7.31 (AA'XX' type, 8H, 2x C_6H_4Cl)	440	313 (35200)
5c	Br	1590, 1567, 1525, 1494, 1479, 1456, 1356, 1287, 1184, 1103, 1066, 1003, 918, 888, 831, 541, 510	(DMSO-d_6) 4.43 (s, 4H, N-CH_2CH_2N), 6.92-7.52 (AA'XX' type, 8H, 2x C_6H_4Br)	592	313 (19600)
5d	H	1586, 1531, 1485, 1454 1358, 1285, 1189, 767, 697	($CDCl_3$) 4.60 (s, 4H, NCH_2-CH_2N), 6.90-7.40 (m, 10H, 2x NC_6H_5)	371	311 (26400)
5e	CH_3	1584, 1526, 1501, 1445, 1355, 1283, 1213, 1182, 1110, 916, 834, 820, 715, 622, 545, 521	($CDCl_3$) 2.33 (s, 6H, 2x C_6H_4-CH_3), 4.59 (s, 4H, N-CH_2CH_2N), 6.95-7.15 (AA'XX' type, 8H, 2x C_6H_4-CH_3)	399	312 (17600)
5f	CH_3O	1602, 1588, 1537, 1501, 1454, 1351, 1293, 1282, 1247, 1182, 1164, 1106, 1028, 837, 628, 582, 408	(DMSO-d_6) 3.73 (s, 6H, 2x C_6H_4-OCH_3), 4.42 (s, 4H, NCH_2CH_2N), 6.87-7.01 (AA'XX' type, 8H, 2x C_6H_4-OCH_3)	431	311 (32000)



5

a: R = NO$_2$ **c**: R = Br **e**: R = CH$_3$
b: R = Cl **d**: R = H **f**: R = CH$_3$O

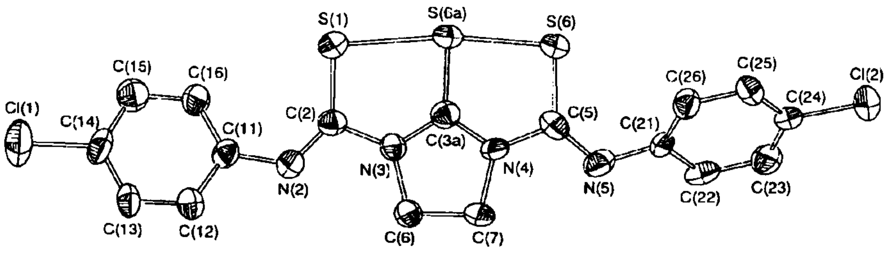


Figure 1. Molecular structure of **5b** with numbering of the non-H atoms.

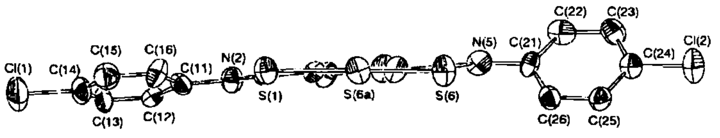


Figure 2. Molecular structure of **5b** viewed along S(6a)-C(3a) bond.

of two p-ClC$_6$H$_4$ groups at the imino nitrogens is *syn* to the S-C bond. The trithiadiazapentalene ring containing N(2), C(6), C(7) and N(5) is almost planar (Figure 2).

Possible Pathway for the Formation of 5a-f.

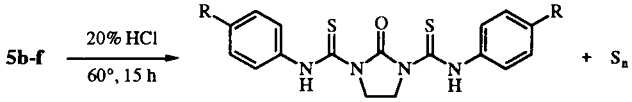
Scheme 1 shows a possible pathway for the formation of **5a-f**. The reaction is initiated by an electrophilic attack of bromine on the sulfur atom of the 2-imidazolidinethione ring of **3**. The successive formation of the S-S bonds *via* **6** and **7** give the hydrobromide salt **8** of the trithiadiazapentalene derivatives. The treatment of **8** with an aqueous sodium bicarbonate gives **5**. The formation of **8** was also confirmed by a separate experiment using **5e**.

Ring-opening Reaction of Trithiadiazapentalene Derivatives under Acidic Conditions.

Heating of **5b** in 20% hydrochloric acid at 60° for 15 hours gave 1,3-bis(p-chlorophenylthiocarbamoyl)-2-imidazolidinone (**9b**) in 87% yield, accompanied by the production of sulfur in the same amount as that of **9b**. In a similar manner, **5c-f** also were converted into **9c-f**, respectively, with production of sulfur, being similar to the ring-opening reaction with 10-*S*-3 tetraazapentalenes [5]. The structure of the products was determined by their ir and ^{1}H nmr spectra, and elemental analysis. The yields and

Selected Bond Length (Å) and Angle (°)

S(1)-S(6a)	2.488(3)
S(6a)-C(3a)	1.720(13)
S(1)-C(2)	1.716(13)
N(3)-C(2)	1.420(10)
N(3)-C(3a)	1.346(10)
N(2)-C(2)	1.284(11)
S(1)-S(6a)-S(6)	170.3(2)
S(1)-S(6a)-C(3a)	83.7(4)
S(6a)-S(1)-C(2)	95.3(4)
C(3a)-N(3)-C(2)	125.6(10)
S(6a)-C(3a)-N(3)	124.1(9)
S(1)-C(2)-N(3)	110.0(8)



9

b: R = Cl **e**: R = CH$_3$
c: R = Br **f**: R = CH$_3$O
d: R = H

Scheme 1

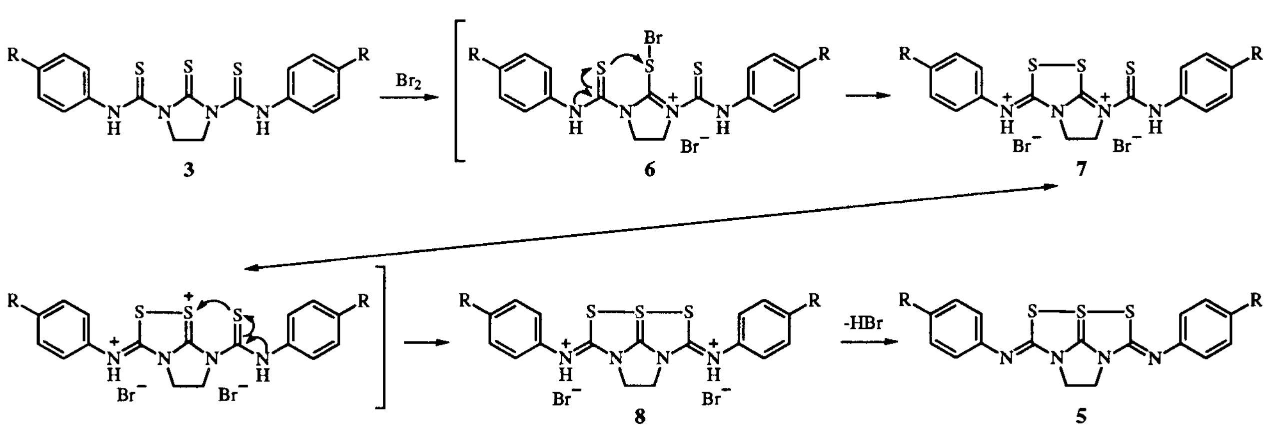
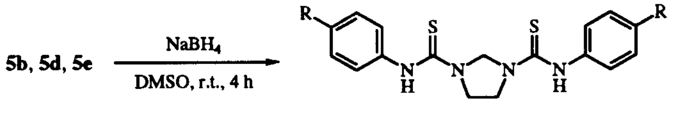


Table 5

The Ring-Opening Reactions of the Trithiadiazapentalene Derivatives **5b-f** under Acidic Conditions [a]

Trithiadiazapentalene	Product	Mp (°)	Yield (%) [b]
5b	**9b**	200-201	87
5c	**9c**	201-203	90
5d	**9d**	201-203	98
5e	**9e**	218-219	96
5f	**9f**	202-203	85

[a] The reactions were carried out in 20% hydrochloric acid at 60°.
[b] Isolated yields were based on **5b-f**.



13

b: R = Cl
d: R = H
e: R = CH_3

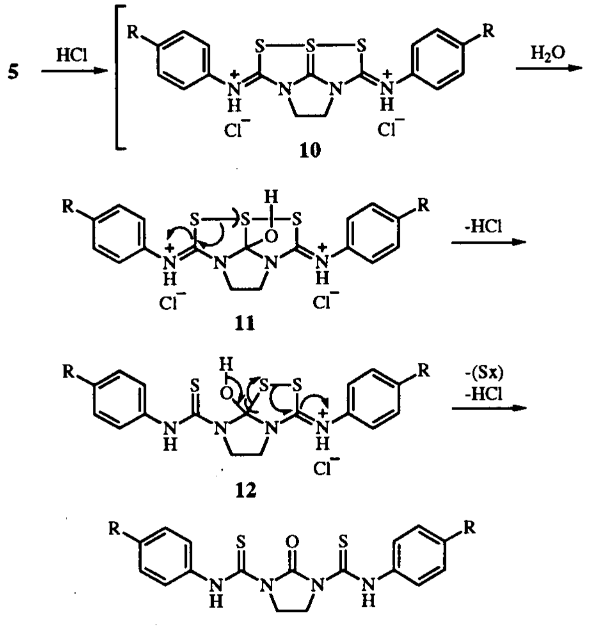
Table 6

Reaction of **5b**, **5d**, and **5e** with Sodium Borohydride [a]

Trithiadiazapentalene	Product	Yield (%) [b]
5b (R = Cl)	**13b**	61
5d (R = H)	**13d**	50
5e (R = CH_3)	**13e**	47

[a] The reactions were carried out in DMSO at room temperature for 4 hours. [b] Isolated yields were based on **5b**, **5d**, and **5e**, respectively.

Scheme 2



9

melting points of **9b-f** are summarized in Table 5. Scheme 2 shows a possible pathway for the reaction.

The reaction is probably initiated by the addition of proton on the nitrogen atom at the exocyclic C-N double bonds. The nucleophilic attack of water toward the carbon atom of the C=S^{IV} moiety and a subsequent ring-opening

Table 7

Melting Points and Analyses of Compounds **13b**, **13d**, and **13e**

Compound	R	Mp, °C	Molecular Formula	Analysis % Calcd./Found C	H	N
13b	Cl	186-187	$C_{17}H_{16}N_4S_2Cl_2$	49.63 49.37	3.92 3.73	13.62 13.38
13d	H	189.5-190.5	$C_{17}H_{18}N_4S_2$	59.61 59.36	5.30 5.16	16.36 16.20
13e	CH_3	197-198	$C_{19}H_{22}N_4S_2$	61.58 61.64	5.98 6.08	15.12 15.23

Table 8

Spectral Data of Compounds **13b**, **13d**, and **13e**

Compound	R	IR (cm^{-1}) (Potassium Bromide)	^{1}H NMR (δ, ppm) (DMSO-d_6)	FAB MS (M+H)$^+$, m/z
13b	Cl	3337, 1585, 1524, 1493, 1468, 1411, 1382, 1334, 1292, 1091, 1014, 827, 777	4.08 (s, 4H, NCH_2CH_2N), 5.37 (s, 2H, NCH_2N), 7.40-7.45 (m, 8H, 2x NH-C_6H_4-Cl), 9.40 (br s, 2H, 2x NH)	343
13d	H	3331, 3258, 1594, 1528, 1498, 1450, 1392, 1344, 1294, 1241, 962, 760, 696, 486	4.08 (s, 4H, NCH_2CH_2N), 5.39 (s, 2H, NCH_2N), 7.13-7.41 (m, 10H, 2x NH-C_6H_5), 9.33 (br s, 2H, 2x NH)	371
13e	CH_3	3319, 1590, 1523, 1460, 1428, 1414, 1383, 1338, 1294, 1223, 959, 814, 736	2.29 (s, 6H, 2x C_6H_4-CH_3), 4.05 (s, 4H, NCH_2CH_2N), 5.35 (s, 2H, NCH_2N), 7.17-7.26 (AA'XX' type, 8H, 2x NH-C_6H_4-CH_3), 9.25 (br s, 2H, 2x NH)	412

led to the formation of **9** and sulfur *via* **11** and **12**.

Reaction of Trithiadiazapentalene Derivatives **5b**, **5d**, and **5e** with Sodium Borohydride.

The reduction of **5b**, **5d**, and **5e** with a large excess of sodium borohydride in dimethyl sulfoxide at room temperature for 4 hours gave the ring-opening products, 1,3-bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidines **13b**, **13d**, and **13e**, respectively, by the reductive elimination of the $C=S^{IV}$ moiety, thus being similar to that in the case of the tetraazapentalene derivatives [6]. The yields are shown in Table 6.

The ^{1}H nmr spectra of **13b**, **13d**, and **13e** exhibited characteristic signals due to the methylene protons at the 2-position in the region of 5.35-5.39 ppm as a singlet. Analytical and spectral data of **13b**, **13d**, and **13e** are shown in Tables 7 and 8.

EXPERIMENTAL

Melting points were determined on a Yanagimoto MP-S3 melting point apparatus and were uncorrected. Proton magnetic resonance (^{1}H nmr) spectra were recorded on a JEOL JNM-GX (270 MHz) using TMS as an internal standard. The ir and uv spectra were determined on a PERKIN ELMER 1600 FT IR spectrometer and Shimadzu UV-160A spectrometer, respectively. Mass spectra were obtained using a JEOL-DX303HF spectrometer with FAB ionization. Elemental analyses were recorded on a Yanagimoto MT-3 CHN recorder. Purifications of products were conducted by column chromatography on silica gel (wakogel C-300) or by preparative tlc on silica gel (Merck Kieselgel 60 GF254).

Preparation of 1,3-Bis(*p*-substituted-phenylthiocarbamoyl)-2-imidazolidinethiones **3a-f**.

A typical procedure: A hexane solution of butyllithium (6.17 mmoles) was added under argon to cooled THF solution (0°, 30 ml) of ethylene thiourea (300 mg, 2.94 mmoles) with stirring at 0°, and the mixture was stirred for 1 hour under the same conditions. A THF solution (10 ml) of *p*-nitrophenylisothiocyanate (1.59 g, 8.82 mmoles) was then added and the resulting mixture was stirred for 3 hours. After THF was evaporated, the residue was poured into an aqueous ammonium chloride solution and the solution was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column with dichloromethane to give 1,3-bis(*p*-nitrophenylthiocarbamoyl)-2-imidazolidinethione **3a** (470 mg, 35%) and 1-(*p*-nitrophenylthiocarbamoyl)-2-imidazolidinethione **4a** (246 mg, 30%). Recrystallization from chloroform-hexane gave an analytically pure compound.

1,3-Bis(*p*-nitrophenylthiocarbamoyl)-2-imidazolidinethione (**3a**) and 1-(*p*-Nitrophenylthiocarbamoyl)-2-imidazolidinethione (**4a**).

These compounds were obtained by the reaction of **2** with *p*-nitrophenylisothiocyanate. (**3a**), mp 134-135°; ir (potassium bromide): 2919, 1620, 1596, 1570, 1549, 1506, 1496, 1480, 1470, 1432, 1405, 1329, 1308, 1205, 1110, 1049, 857, 848, 749, 658, 494 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 4.57 (s, 4H, NCH_2CH_2N), 7.91-8.32 (AA' XX' type, 8H, 2x $N\text{-}C_6H_4\text{-}NO_2$), 13.04 (br s, 2H, 2x NH); uv (dichloromethane): λ max 357 nm (ε 38600).

Anal. Calcd. for $C_{17}H_{14}O_4N_6S_3$: C, 44.14; H, 3.05; N, 18.17. Found: C, 44.09; H, 2.91; N, 18.07.

Compound **4a** had mp 184.5-185.5°; ir (potassium bromide): 3424, 3302, 2773, 1632, 1587, 1530, 1505, 1477, 1420, 1390, 1366, 1332, 1264, 1218, 1186, 1172, 1111, 1038, 927, 862, 852, 752, 529 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.68 (br t, 2H, $NHCH_2CH_2N$, J = 8.9 Hz), 4.69 (t, 2H, $NHCH_2CH_2N$, J = 8.9 Hz), 6.72 (br s, 1H, $CH_2NHC=S$), 7.95-8.27 (AA' XX' type, 4H, $N\text{-}C_6H_4\text{-}NO_2$), 14.34 (br s, 1H, $C_6H_4NHC=S$); uv (dichloromethane): λ max 349 nm (ε 14900), 296 nm (ε 22000).

Anal. Calcd. for $C_{10}H_{10}O_2N_4S_2$: C, 42.53; H, 3.57; N, 19.85. Found: C, 42.52; H, 3.31; N, 19.99.

1,3-Bis(*p*-chlorophenylthiocarbamoyl)-2-imidazolidinethione (**3b**) and 1-(*p*-Chlorophenylthiocarbamoyl)-2-imidazolidinethione (**4b**).

These compounds were obtained from the reaction of **2** with *p*-chlorophenylisothiocyanate.

Compound **3b** had mp 128-129°; ir (potassium bromide): 2932, 1603, 1546, 1491, 1470, 1438, 1400, 1344, 1301, 1209, 1119, 1047, 1010, 921, 824, 801, 755, 670, 499, 453 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 4.54 (s, 4H, NCH_2CH_2N), 7.26-7.56 (AA' XX' type, 8H, 2x $N\text{-}C_6H_4\text{-}Cl$), 12.72 (br s, 2H, 2x NH); uv (dichloromethane): λ max 309 nm (ε 36800).

Anal. Calcd. for $C_{17}H_{14}N_4S_3Cl_2$: C, 46.25; H, 3.20; N, 12.70. Found: C, 46.13; H, 3.01; N, 12.71.

Compound **4b** had mp 184-186°; ir (potassium bromide): 3227, 2924, 1614, 1541, 1493, 1453, 1420, 1398, 1376, 1335, 1305, 1274, 1198, 1115, 1086, 1061, 1043, 1010, 927, 825, 668, 529 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.64 (br t, 2H, $NHCH_2CH_2N$, J = 9.2 Hz), 4.72 (t, 2H, $NHCH_2CH_2N$, J = 8.9 Hz), 6.59 (br s, 1H, $CH_2NHC=S$), 7.34-7.58 (AA' XX' type, 4H, $N\text{-}C_6H_4\text{-}Cl$), 13.80 (br s, 1H, $C_6H_4NHC=S$); uv (dichloromethane): λ max 288 nm (ε 21700), 267 nm (ε 17100).

Anal. Calcd. for $C_{10}H_{10}N_3S_2Cl$: C, 44.19; H, 3.71; N, 15.46. Found: C, 44.25; H, 3.56; N, 15.61.

1,3-Bis(*p*-bromophenylthiocarbamoyl)-2-imidazolidinethione (**3c**) and 1-(*p*-Bromophenylthiocarbamoyl)-2-imidazolidinethione (**4c**).

These compounds were obtained from the reaction of **2** with *p*-bromophenylisothiocyanate.

Compound **3c** had mp 124.5-125.5°; ir (potassium bromide): 3087, 2927, 1613, 1554, 1524, 1490, 1448, 1387, 1350, 1306, 1214, 1110, 1065, 1042, 1007, 921, 816, 796, 758, 725, 637, 493 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 4.54 (s, 4H, NCH_2CH_2N), 7.48-7.57 (m, 8H, 2x $N\text{-}C_6H_4\text{-}Br$), 12.72 (br s, 2H, 2x NH); uv (dichloromethane): λ max 311 nm (ε 28600).

Anal. Calcd. for $C_{17}H_{14}N_4S_3Br_2$: C, 38.45; H, 2.66; N, 10.57. Found: C, 38.49; H, 2.55; N, 10.58.

Compound **4c** had mp 161-163°; ir (potassium bromide): 3238, 2852, 2812, 1622, 1561, 1534, 1488, 1468, 1415, 1394, 1373, 1330, 1305, 1284, 1192, 1114, 1068, 1042, 1002, 925, 824, 735, 652, 632, 601, 500 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.64 (br t, 2H, $NHCH_2CH_2N$, J = 8.9 Hz), 4.72 (t, 2H, $NHCH_2CH_2N$, J = 9.2 Hz), 6.60 (br s, 1H, $CH_2NHC=S$), 7.51-7.53 (m, 4H, $N\text{-}C_6H_4\text{-}Br$), 13.80 (br s, 1H, $C_6H_4NHC=S$); uv (dichloromethane): λ max 287 nm (ε 18700), 266 nm (ε 15300).

Anal. Calcd. for $\mathrm{C_{10}H_{10}N_3S_2Br}$: C, 37.98; H, 3.19; N, 13.29. Found: C, 37.78; H, 3.06; N, 13.19.

1,3-Bis(phenylthiocarbamoyl)-2-imidazolidinethione (**3d**) and 1-(Phenylthiocarbamoyl)-2-imidazolidinethione (**4d**).

These compounds were obtained from the reaction of **2** with phenylisothiocyanate.

Compound **3d** had mp 117-119°; ir (potassium bromide): 3224, 3020, 2932, 1608, 1563, 1524, 1496, 1470, 1459, 1434, 1386, 1343, 1312, 1215, 1127, 1069, 1055, 924, 892, 798, 761, 739, 701, 579, 500 $\mathrm{cm^{-1}}$; ^{1}H nmr (deuteriochloroform): δ 4.56 (s, 4H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 7.29-7.61 (m, 10H, 2x $\mathrm{N\text{-}C_6}H_5$), 12.75 (br s, 2H, 2x NH); uv (dichloromethane): λ max 277 nm (ε 29900), 267 nm (ε 28600).

Anal. Calcd. for $\mathrm{C_{17}H_{16}N_4S_3}$: C, 54.80; H, 4.32; N, 15.04. Found: C, 54.78; H, 4.21; N, 15.33.

Compound **4d** had mp 176-177°; ir (potassium bromide): 3289, 2862, 1621, 1597, 1568, 1537, 1519, 1498, 1476, 1466, 1407, 1365, 1332, 1261, 1218, 1190, 1180, 1077, 1059, 1027, 925, 764, 739, 691, 591, 504 $\mathrm{cm^{-1}}$; ^{1}H nmr (deuteriochloroform): δ 3.64 (br t, 2H, $\mathrm{NHC}H_2\mathrm{CH_2N}$, J = 9.5 Hz), 4.74 (t, 2H, $\mathrm{NHCH_2C}H_2\mathrm{N}$, J = 8.9 Hz), 6.55 (br s, 1H, $\mathrm{CH_2N}H\mathrm{C{=}S}$), 7.22-7.61 (m, 5H, $\mathrm{N\text{-}C_6}H_5$), 13.75 (br s, 1H, $\mathrm{C_6H_5N}H\mathrm{C{=}S}$); uv (dichloromethane): λ max 289 nm (ε 19600), 265 nm (ε 15700).

Anal. Calcd. for $\mathrm{C_{10}H_{11}N_3S_2}$: C, 50.60; H, 4.61; N, 17.71. Found: C, 50.56; H, 4.54; N, 17.81.

1,3-Bis(*p*-tolylthiocarbamoyl)-2-imidazolidinethione (**3e**) and 1-(*p*-Tolylthiocarbamoyl)-2-imidazolidinethione (**4e**).

These compounds were obtained from the reaction of **2** with *p*-tolylisothiocyanate.

Compound **3e** had mp 136-137°; ir (potassium bromide): 3161, 3102, 2916, 1607, 1552, 1512, 1446, 1407, 1352, 1316, 1209, 1182, 1116, 1072, 1046, 919, 814, 748, 719, 670, 502 $\mathrm{cm^{-1}}$; ^{1}H nmr (deuteriochloroform): δ 2.33 (s, 6H, 2x $\mathrm{C_6H_4\text{-}C}H_3$), 4.55 (s, 4H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 7.22-7.46 (AA' XX' type, 8H, 2x $\mathrm{N\text{-}C_6}H_4\mathrm{\text{-}CH_3}$), 12.48 (br s, 2H, 2x NH); uv (dichloromethane): λ max 308 nm (ε 33400).

Anal. Calcd. for $\mathrm{C_{19}H_{20}N_4S_3}$: C, 56.96; H, 5.03; N, 13.99. Found: C, 56.90; H, 5.18; N, 13.95.

Compound **4e** had mp 175.5-177.5°; ir (potassium bromide): 3234, 2907, 1621, 1563, 1541, 1511, 1467, 1400, 1372, 1330, 1295, 1203, 1120, 1059, 1044, 925, 819, 736, 550, 508, 494 $\mathrm{cm^{-1}}$; ^{1}H nmr (deuteriochloroform): δ 2.35 (s, 3H, $\mathrm{N\text{-}C_6H_4\text{-}C}H_3$), 3.63 (br t, 2H, $\mathrm{NHC}H_2\mathrm{CH_2N}$, J = 8.9 Hz), 4.70 (t, 2H, $\mathrm{NHCH_2C}H_2\mathrm{N}$, J = 9.2 Hz), 6.58 (br s, 1H, $\mathrm{CH_2N}H\mathrm{C{=}S}$), 7.18-7.45 (AA' XX' type, 4H, $\mathrm{N\text{-}C_6}H_4\mathrm{\text{-}CH_3}$), 13.64 (br s, 1H, $\mathrm{C_6H_4N}H\mathrm{C{=}S}$); uv (dichloromethane): λ max 288 nm (ε 24300), 266 nm (ε 18500).

Anal. Calcd. for $\mathrm{C_{11}H_{13}N_3S_2}$: C, 52.55; H, 5.21; N, 16.72. Found: C, 52.70; H, 4.91; N, 16.87.

1,3-Bis(*p*-methoxyphenylthiocarbamoyl)-2-imidazolidinethione (**3f**) and 1-(*p*-Methoxyphenylthiocarbamoyl)-2-imidazolidinethione (**4f**).

These compounds were obtained from the reaction of **2** with *p*-methoxyphenylisothiocyanate.

Compound **3f** had mp 131.5-133°; ir (potassium bromide): 3106, 3000, 2954, 2833, 1618, 1596, 1564, 1534, 1509, 1462, 1435, 1400, 1350, 1303, 1248, 1218, 1176, 1076, 1049, 1028, 920, 823, 750, 549, 514 $\mathrm{cm^{-1}}$; ^{1}H nmr (deuteriochloroform): δ 3.83 (s, 6H, 2x $\mathrm{C_6H_4\text{-}OC}H_3$), 4.55 (s, 4H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 6.94-7.48 (AA' XX' type, 8H, 2x $\mathrm{N\text{-}C_6}H_4\mathrm{\text{-}OCH_3}$), 12.62 (br s, 2H, 2x NH); uv (dichloromethane): λ max 307 nm (ε 34300).

Anal. Calcd. for $\mathrm{C_{19}H_{20}O_2N_4S_3}$: C, 52.75; H, 4.66; N, 12.95. Found: C, 52.65; H, 4.82; N, 13.24.

Compound **4f** had mp 164-165°; ir (potassium bromide): 3321, 3119, 2976, 2917, 2841, 1598, 1558, 1528, 1510, 1463, 1426, 1379, 1336, 1295, 1246, 1233, 1209, 1191, 1168, 1020, 931, 820, 653, 568, 518 $\mathrm{cm^{-1}}$; ^{1}H nmr (deuteriochloroform): δ 3.63 (br t, 2H, $\mathrm{NHC}H_2\mathrm{CH_2N}$, J = 9.2 Hz), 3.82 (s, 3H, $\mathrm{N\text{-}C_6H_4\text{-}OC}H_3$), 4.73 (t, 2H, $\mathrm{NHCH_2C}H_2\mathrm{N}$, J = 8.9 Hz), 6.59 (br s, 1H, $\mathrm{CH_2N}H\mathrm{C{=}S}$), 6.91-7.46 (AA' XX' type, 4H, $\mathrm{N\text{-}C_6}H_4\mathrm{\text{-}OCH_3}$), 13.56 (br s, 1H, $\mathrm{C_6H_4N}H\mathrm{C{=}S}$); uv (dichloromethane): λ max 286 nm (ε 22300).

Anal. Calcd. for $\mathrm{C_{11}H_{13}N_3OS_2}$: C, 49.41; H, 4.90; N, 15.72. Found: C, 49.23; H, 4.80; N, 15.71.

Reaction of **3** with Bromine.

A typical procedure: Bromine (29 mg, 0.18 mmole) in dichloromethane (10 ml) was added under argon to a dichloromethane solution (150 ml) of **3a** (84 mg, 0.18 mmole) at room temperature. After stirring for 10 minutes, the mixture was poured into aqueous sodium bicarbonate solution and the solution was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate and concentrated to about 50 ml under reduced pressure. The precipitate was collected and washed with *n*-hexane.

X-ray Analysis Data for **5b**.

Crystals were grown from hexane-dichloromethane: $\mathrm{C_{17}H_{12}N_4S_3Cl_2}$, Fw = 439.41, triclinic, space group $P\bar{1}$, a = 8.753(1), b = 11.173(1), c = 11.194(1) Å, α = 110.1(3), β = 103.8(2), γ = 106.0(1)°, V = 918(2) Å^3, Z = 2, Dx = 1.589 $\mathrm{Mgm^{-3}}$, μ(MoKα) = 0.690 $\mathrm{mm^{-1}}$. A yellow crystal with dimensions of 0.08 x 0.03 x 0.15 mm was used for data collection on a Mac-Science DIP-3000 diffractometer (a rapid X-ray measurement system with Imaging Plates) with graphite monochromatized MoKα radiation (λ = 0.71073 Å). 3394 unique reflections were obtained up to 2θ of 52° and 2084 observed reflections ($|F|>3\sigma(F)$) were used for refinement. The structure was solved by a direct method using MULTAN78 [7] and successive Fourier syntheses and refined by the block-diagonal least-squares method using UNICSIII [8] to give R = 0.102 and wR = 0.104. Selected bond lengths (Å) and angles (°): S(1)-S(6a) 2.488(3), S(6)-S(6a), 2.314(4), S(6a)-C(3a) 1.720(13), S(1)-C(2) 1.716(13), S(6)-C(5) 1.757(13), N(3)-C(2) 1.420(14), N(3)-C(3a) 1.346(10), S(1)-S(6a)-S(6) 170.3(2), S(1)-S(6a)-C(3a) 83.7(4), S(6)-S(6a)-C(3a) 86.7(4), S(6a)-S(1)-C(2) 95.3(4), S(6a)-S(6)-C(5) 94.8(4), C(2)-N(2)-C(11) 125.7(11), C(3a)-N(3)-C(2) 125.6(10), C(3a)-N(4)-C(5) 122.7(10).

2,3,4,5-Tetrahydro-2,5-bis(*p*-tolylimino)-3,4-ethano-1,6,6aλ4-trithia-3,4-diazapentalene Hydrobromide (**5e**).

To a dichloromethane solution (15 ml) of **3e** (95 mg, 0.24 mmole) was added a dichloromethane solution (10 ml) of bromine (38 mg, 0.24 mmole) under argon at room temperature, and the mixture was stirred for 10 minutes. The resulting precipitate was collected and washed with *n*-hexane to give **5e** in 92% (122 mg) yield, mp 232-234° dec; ir (potassium bromide): 3424, 3364, 2730, 1588, 1568, 1524, 1506, 1387, 1306, 818, 711, 660, 406 $\mathrm{cm^{-1}}$; ^{1}H nmr (DMSO-d$_6$): δ 2.29 (s, 6H, 2x $\mathrm{C_6H_4\text{-}C}H_3$), 4.50 (s, 4H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 6.94-7.19 (AA' XX' type, 8H, 2x N-

C_6H_4-CH_3).

Anal. Calcd. for $C_{19}H_{20}N_4S_3Br_2$: C, 40.72; H, 3.60; N, 10.00. Found: C, 40.84; H, 3.76; N, 9.77.

Ring-Opening Reaction of Trithiadiazapentalene Derivatives under Acidic Conditions.

Typical procedure: Compound **5c** (50 mg, 0.095 mmole) was stirred in 20% hydrochloric acid (20 ml) at 60° for 15 hours. After cooling to room temperature, the reaction mixture was poured into water. The solution was extracted several times with dichloromethane. The dichloromethane layer was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column with dichloromethane/*n*-hexane (1:1) to give 44 mg (90%) of **9c**.

1,3-Bis(*p*-chlorophenylthiocarbamoyl)-2-imidazolidinone (**9b**).

This compound was obtained by the ring-opening reaction of **5b**, mp 200-201°; ir (potassium bromide): 3266, 3178, 3085, 1690, 1604, 1559, 1518, 1494, 1469, 1387, 1254, 1170, 1097, 1085, 1013, 926, 824, 742, 492 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.32 (s, 4H, NCH_2CH_2N), 7.35-7.58 (AA' XX' type, 8H, 2x NH-C_6H_4-Cl), 11.62 (br s, 2H, 2x, NH); uv (dichloromethane): λ max 281 nm (ε 43100).

Anal. Calcd. for $C_{17}H_{14}ON_4S_2Cl_2$: C, 48.00; H, 3.31; N, 13.18. Found: C, 47.82; H, 3.11; N, 13.35.

1,3-Bis(*p*-bromophenylthiocarbamoyl)-2-imidazolidinone (**9c**).

This compound was obtained by the ring-opening reaction of **5c**, mp 201-203°; ir (potassium bromide): 3257, 3080, 1692, 1603, 1557, 1518, 1490, 1469, 1386, 1253, 1170, 1096, 1075, 1010, 962, 820, 744, 496 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.32 (s, 4H, NCH_2CH_2N), 7.48-7.56 (m, 8H, 2x NH-C_6H_4-Br), 11.62 (br s, 2H, 2x, NH); uv (dichloromethane): λ max 281 nm (ε 49600).

Anal. Calcd. for $C_{17}H_{14}ON_4S_2Br_2$: C, 39.70; H, 2.74; N, 10.90. Found: C, 39.50; H, 2.50; N, 10.92.

1,3-Bis(phenylthiocarbamoyl)-2-imidazolidinone (**9d**).

This compound was obtained by the ring-opening reaction of **5d**, mp 201-203°; ir (potassium bromide): 3262, 3188, 3078, 1693, 1605, 1567, 1540, 1482, 1470, 1390, 1364, 1315, 1248, 1170, 1096, 960, 767, 751, 690, 576 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.33 (s, 4H, NCH_2CH_2N), 7.28-7.61 (m, 10H, 2x NH-C_6H_5), 11.65 (br s, 2H, 2x, NH); uv (dichloromethane): λ max 277 nm (ε 43500).

Anal. Calcd. for $C_{17}H_{16}ON_4S_2$: C, 57.27; H, 4.52; N, 15.72. Found: C, 56.99; H, 4.27; N, 15.78.

1,3-Bis(*p*-tolylthiocarbamoyl)-2-imidazolidinone (**9e**).

This compound was obtained by the ring-opening reaction of **5e**, mp 218-219.5°; ir (potassium bromide): 3071, 1706, 1620, 1609, 1563, 1513, 1474, 1419, 1389, 1319, 1253, 1167, 1090, 964, 819, 756, 732, 509 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.37 (s, 6H, 2x C_6H_4-CH_3), 4.32 (s, 4H, NCH_2CH_2N), 7.20-7.45 (AA' XX' type, 8H, 2x NH-C_6H_4-CH_3), 11.55 (br s, 2H, 2x, NH); uv (dichloromethane): λ max 277 nm (ε 44900).

Anal. Calcd. for $C_{19}H_{20}ON_4S_2$: C, 59.34; H, 5.24; N, 14.57. Found: C, 59.26; H, 4.97; N, 14.68.

1,3-Bis(*p*-methoxyphenylthiocarbamoyl)-2-imidazolidinone (**9f**).

This compound was obtained by the ring-opening reaction of **5f**, mp 202-203°; ir (potassium bromide): 3071, 1698, 1616, 1560, 1511, 1462, 1421, 1390, 1364, 1304, 1240, 1174, 1095, 1026, 820, 760, 544 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.82 (s, 6H, 2x C_6H_4-OCH_3), 4.32 (s, 4H, NCH_2CH_2N), 6.92-7.45 (AA' XX' type, 8H, 2x NH-C_6H_4-OCH_3), 11.47 (br s, 2H, 2x, NH); uv (dichloromethane): λ max 279 nm (ε 45500).

Anal. Calcd. for $C_{19}H_{20}O_3N_4S_2$: C, 54.78; H, 4.84; N, 13.45. Found: C, 54.55; H, 4.60; N, 13.48.

Reduction of Trithiadiazapentalene Derivatives **5** with Sodium Borohydride.

A typical procedure: To a solution of **5b** (30 mg, 0.0683 mmole) in DMSO (30 ml) was added 20 equivalents of sodium borohydride (52 mg, 1.37 mmoles). The reaction mixture was stirred at room temperature for 4 hours, poured into water, and the solution was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate and concentrated to 30 ml under reduced pressure. The precipitate was collected and washed with *n*-hexane to obtain **13b**.

Acknowledgements.

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 04504002 and No. 06640696) from the Ministry of Science, Culture and Education of Japan, which is gratefully acknowledged.

REFERENCES AND NOTES

[1a] N. Lozac'h, *Adv. Heterocyclic Chem.*, **13**, 161 (1971); [b] A. S. Ingram, D. H. Reid, and J. D. Symon, *J. Chem. Soc., Perkin Trans. 1*, 242 (1974); [c] K. Akiba and N. Inamoto, *Kagaku No Ryoiki, Zokan*, **124**, 93 (1980); [d] M. Yokoyama, T. Shiraishi, H. Hatanaka, and K. Ogata, *J. Chem. Soc., Chem. Commun.*, 1704 (1985); [e] K. Akiba, *Nippon Kagaku Kaishi*, 1130 (1987).

[2a] R. J. S. Beer and A. Naylor, *Tetrahedron Letters*, 2989 (1973); [b] R. J. S. Beer, N. H. Holmes, and A. Naylor, *J. Chem. Soc., Perkin Trans. 1*, 2909 (1979).

[3a] N. Matsumura, M. Tomura, R. Mando, Y. Tsuchiya, and S. Yoneda, *Bull. Chem. Soc. Japan*, **59**, 3693 (1986); [b] N. Matsumura, M. Tomura, O. Mori, Y. Tsuchiya, S. Yoneda, and K. Toriumi, *Bull. Chem. Soc. Japan*, **61**, 2419 (1988); [c] N. Matsumura, M. Tomura, O. Mori, Y. Takamura, and S. Yoneda, *Tetrahedron Letters*, 2259 (1989); [d] N. Matsumura, R. Hirase, O. Mori, and H. Inoue, *Chem. Letters*, 865 (1993); [e] N. Matsumura, R. Hirase, and H. Inoue, *Tetrahedron Letters*, 899 (1994).

[4] C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.

[5] M. Tomura, N. Matsumura, O. Mori, H. Chikusa, S. Kamitani, and H. Inoue, *J. Heterocyclic Chem.*, **27**, 2215 (1990).

[6] N. Matsumura, M. Tomura, O. Mori, M. Ukawa, and S. Yoneda, *Heterocycles*, 3097 (1987).

[7] P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, MULTAN78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, England and Louvain-la-Nerve, Belgium, 1987.

[8] T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).