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The reaction of 5-bromomethyl-3-(*p*-bromomethylphenyl)isoxazole with *o*-, *m*-, and *p*-bis(mercaptomethyl)benzenes gave the corresponding dithia- and/or tetrathiaisoxazolophanes, whose relative yields strongly depended upon the nature of the mercaptomethyl compound. The above isoxazole dibromide reacted with the bis(mercaptomethyl)isoxazole to afford a mixture of two isomeric dithiaisoxazolophanes.

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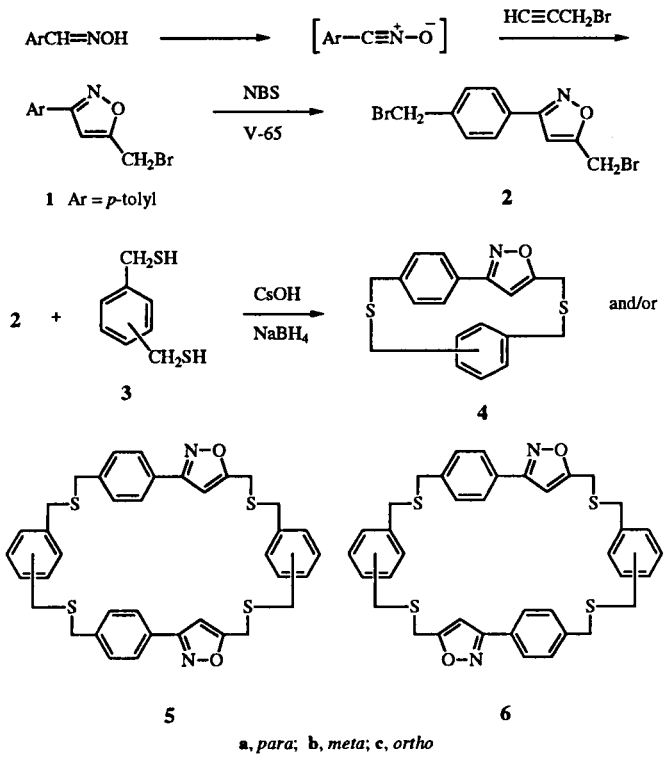
There has been much work on the synthesis and conformational behavior of macrocyclic π-excessive and π-deficient heterophanes [1]. Since heterocycles are known as latent functional group equivalents [2], the conversion of a heterocyclic ring in a heterophane into the corresponding functional group(s) may provide a promising route to a cyclophane bearing functional group(s) in its bridge. In fact, conversion of furanophanes [3] and 1,2,5-thiadiazolophanes [4] into corresponding 1,4- and 1,2-diketocyclophanes has been reported, respectively. Although an isoxazole moiety is a synthetic equivalent of a 1,3-dicarbonyl group, few macrocyclic compounds incorporating isoxazole units have been reported in the literature [5]. Our continued interest in heterocyclophanes [4,6,7] was directed to new cyclophanes incorporating isoxazole units. In this paper, we describe the synthesis of new thiacyclophanes containing one or two isoxazole units.

Scheme 1



Results and Discussion.

Condensation of 5-Bromomethyl-3-(*p*-bromomethylphenyl)isoxazole with Bis(mercaptomethyl)benzenes.

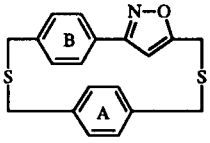
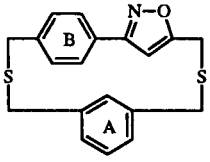
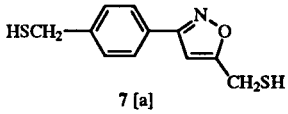
The key starting material, 5-bromomethyl-3-(*p*-bromomethylphenyl)isoxazole **2** was prepared by the bromination of 5-bromomethyl-3-(*p*-tolyl)isoxazole **1**, which was obtained *via* the 1,3-dipolar cycloaddition reaction of nitrile oxide generated from *p*-tolualdoxime with propargyl bromide. Coupling of dibromide **2** with *p*-bis(mercaptomethyl)benzene **3a** in ethanol containing cesium hydroxide and sodium borohydride was performed under high dilution conditions, and after chromatography 1:1 condensed-ring compound **4a** and 2:2 condensed-ring compound **5a** were obtained in 17 and 10% yields, respectively. Under the similar conditions, dibromide **2** reacted with *m*-bis(mercaptomethyl)benzene **3b** to give a 12% yield of 2:2 condensed-ring compound **6b**, along with a small amount of 1:1 condensed-ring compound **4b**. As described below, a condensation mode for 2:2 condensed-ring compound **6b** is different from that for **5a**. In the condensation of dibromide **2** with *o*-bis(mercaptomethyl)benzene **3c**, however, no 1:1 condensed-ring compound **4c** was formed, but instead two 2:2 condensed-ring compounds, **5c** and **6c**, were isolated in 21 and 52% yields, respectively (Scheme 1).

On the basis of spectral and microanalytical data, the 1:1 condensed-ring compounds **4a** and **4b** were characterized as 2,11-dithia[3]paracyclo[3]paracyclo[0](3,5)isoxazolophane and 2,11-dithia[3]metacyclo[3]paracyclo[0](3,5)isoxazolophane, respectively.

The ^{1}H-nmr spectral data of 1:1 compounds, **4a** and **4b**, and a reference compound, 5-mercaptomethyl-3-(*p*-mercaptomethylphenyl)isoxazole **7**, which was readily prepared from **2** as described below (Scheme 2), are shown in Table 1. Both the 1:1 condensed-ring compounds **4a** and **4b** undergo conformational change in solution at room temperature, because all the bridge protons are observed as a singlet. The isoxazole ring protons in both the 1:1 condensed-ring compounds, particularly **4a**, are observed at an appreciable upfield compared with the corresponding signal of **7**; this upfield shift is presumably attributed to the shielding effect of the opposite benzene

Table 1

^{1}H-NMR Spectral Data for **4a**, **4b**, and **7** in Deuteriochloroform (δ: ppm)

Compound	CH_2	4-H in the isoxazole ring	ArH
 **4a**	3.53, 3.68, 3.81, 3.90 (each *s*, 2H)	5.61 (*s*, 1H)	6.62, 6.68 (each d, 2H, J = 8.6 Hz, A ring), 7.17, 7.22 (each d, 2H, J = 8.6 Hz, B ring)
 **4b**	3.34, 3.49, 3.88, 3.93 (each *s*, 2H)	5.90 (*s*, 1H)	6.12 (br s, 1H, inner *H* in A ring), 6.95-7.15 (m, 3H, A ring), 7.19 (*s*, 4H, B ring)
 **7** [a]	3.77 (d, 2H, J = 7.6 Hz), 3.83 (dd, 2H, J = 8.3, 0.7 Hz)	6.49 (d, 1H, J = 0.7 Hz)	7.41, 7.74 (each d, 2H, J = 8.6 Hz)

[a] Chemical shifts of SH protons of **7**: δ 1.80 (t, 1H, J = 7.6 Hz), 2.10 (t, 1H, J = 8.3 Hz).

ring A, respectively. The protons in A ring of **4a** show slight upfield shifts compared with the corresponding signal of *p*-xylene (δ = 6.98) [8]. On the other hand, the inner proton signal (δ = 6.12) in A ring of **4b** shows a remarkable upfield shift compared with the corresponding signal of *m*-xylene (δ = 6.89) [9] and the outer protons signals which are little affected by the anisotropic effects of the opposite arene rings are in the usual range for *m*-xylene (δ = 6.88-7.05) [9].

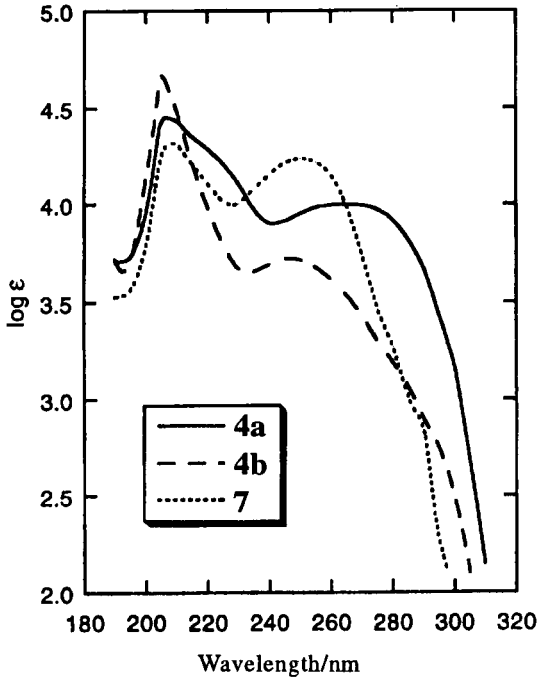


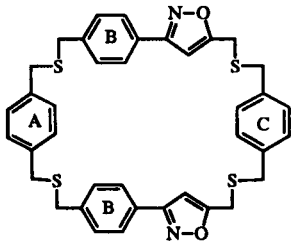
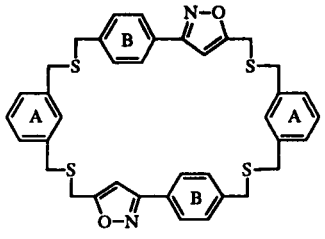
Figure 1. Electronic spectra of **4a**, **4b**, and **7** in ethanol.

The uv spectra of **4a**, **4b** and **7** in ethanol are shown in Figure 1. Significant reduction in extinction and slight hypsochromic shift for **4b** in the region above 230 nm as compared with **7** in the corresponding region are observed. On the other hand, the absorption band of **4a** exhibited a significant bathochromic shift as compared with that of **7**, although a slight reduction in extinction is observed. These facts suggest that the isoxazole ring and the benzene ring B of large 1:1 condensed ring compound **4a** can take a more planar conformation as compared with those of small 1:1 condensed-ring compound **4b**; this consideration is also supported by ^{1}H nmr spectral data described above.

The ^{1}H- and ^{13}C-nmr spectral data of 2:2 condensed-ring compounds **5a** and **6b** are shown in Table 2. In **5a** the protons (δ = 7.07) in A ring are not equivalent with those (δ = 7.19) in C ring and 8 signals for carbons of benzene ring appear in ^{13}C-nmr spectrum; **5a** was thus assigned as 2,11,25,34-tetrathia[3]paracyclo[3](5,3)isoxazolo[0]paracyclo[3]paracyclo[3]paracyclo[0](3,5)isoxazolophane. On the other hand, **6a** was assigned as 2,11,25,34-tetrathia[3]metacyclo[3]paracyclo[0](3,5)isoxazolo[3]metacyclo[3]paracyclo[0](3,5)isoxazolophane derived from a diffrent condensation mode from that for **5a** because two rings A and C are equivalent. Similarly, 2:2 condensed-ring compounds **5c** and **6c** were assumed to be 2,11,25,34-tetrathia[3]orthocyclo[3](5,3)isoxazolo[0]paracyclo[3]-orthocyclo[3]paracyclo[0](3,5)isoxazolophane and

Table 2

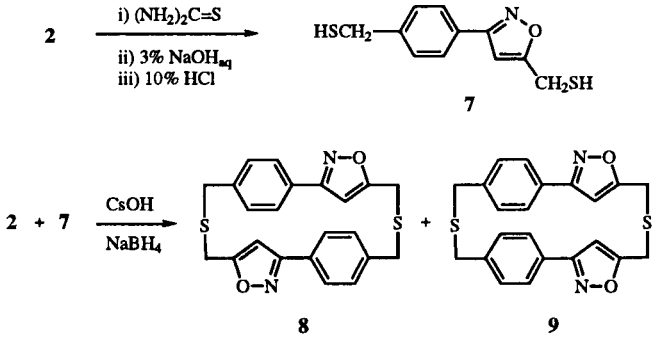
^{1}H- and ^{13}C-NMR Spectral Data for **5a** and **6b** in DMSO-d_6 (δ: ppm)

Compound	NMR	CH_2	Isoxazole ring	Benzene ring
 **5a**	^{1}H	3.60, 3.64, 3.69, 3.72 (each s, 4H)	6.48 (s, 2H)	7.07 (s, 4H, A ring), 7.19 (s, 4H, C ring), 7.16, 7.62 (each d, 4H, J = 8.3 Hz, B ring)
	^{13}C	25.1, 34.6, 35.0, 35.2	100.5 (4-*C*), 161.2 (3-*C*), 170.3 (5-*C*)	126.2, 126.6, 128.6, 128.9, 129.2, 136.5, 136.8, 140.9
 **6b**	^{1}H	3.59, 3.65, 3.82, 3.84 (each s, 4H)	6.7 (s, 2H)	7.12 (s, 2H, inner *H* in A ring), 7.20-7.40 (m, 10H, A and B ring), 7.75 (d, 4H, J = 8.3 Hz, B ring)
	^{13}C (80°)	25.3, 34.8, 35.0, 35.7	100.4 (4-*C*), 161.6 (3-*C*), 170.6 (5-*C*)	126.6, 127.2, 127.4, 127.6, 128.7, 129.3, 129.5, 137.7, 138.2, 140.5

2,11,25,34-tetrathia[3]orthocyclo[3]paracyclo[0](3,5)-isoxazolo[3]orthocyclo[3]paracyclo[0](3,5)isoxazolophane, respectively.

Condensation of dibromide **2** with 5-mercaptomethyl-3-(*p*-mercaptomethylphenyl)isoxazole **7**, which readily prepared from **2**, was next performed under the similar high dilution conditions: A mixture of two isomeric 1:1 condensed-ring compounds, 2,16-dithia[3]paracyclo-[0](3,5)isoxazolo[3]paracyclo[0](3,5)isoxazolophane **8**, and 2,16-dithia[3](5,3)isoxazolo[0]paracyclo[3]paracyclo[0](3,5)isoxazolophane **9** was obtained in 47% yield (Scheme 2). Although attempts to isolate **8** and **9** were unsuccessful, the **8/9** ratio in the mixture was determined to be 2.4/1 by the ^{1}H-nmr spectral study. The isoxazole protons in **8** and **9** appear at δ 5.48 (1.4H, s) and 6.17 (0.6H, s), respectively; the proton in symmetrical structure **8** is much more subject to a shielding effect of the opposite arene than that in the unsymmetrical structure **9**.

Scheme 2



EXPERIMENTAL

All melting points were determined on a Yanagimoto micro-apparatus and are uncorrected. Mass spectra were obtained on a Nippon Densi JMS-AX500 mass spectrometer at 70 eV using a direct inlet system. The ^{1}H- and ^{13}C-nmr spectra were recorded on a Nippon Densi JNM-EX90 and JNM-EX270 spectrometer using tetramethylsilane as an internal standard. The electronic spectra were recorded on a Hitachi 220A spectrophotometer. Column chromatography was carried out on silica gel (Wako gel, C-300). Elemental analyses were performed on a Yanagimoto CHN corder MT-5.

5-Bromomethyl-3-(*p*-tolyl)isoxazole **1**.

A 5% aqueous sodium hypochlorite (220 ml) was added dropwise to a well-stirred solution of *p*-tolualdoxime (10.0 g, 74.1 mmoles), propargyl bromide (10.6 g, 89.1 mmoles) and triethyl amine (75 mg, 0.74 mmole) in dichloromethane (200 ml) at 0° over a 9-hour period. After stirring for 1 hour at room temperature, the reaction phases were separated and the aqueous phase was extracted with dichloromethane. The combined organic layer was washed with water, dried over magnesium sulfate, and the solvent was evaporated *in vacuo* to leave solid, which was recrystallized from *n*-hexane to give 10.6 g (57%) of **1** as colorless needles.

This compound had mp 82-83°; ^{1}H-nmr (deuteriochloroform): δ 2.35 (s, 3H), 4.43 (s, 2H), 6.52 (s, 1H, 4-H in isoxazole ring), 7.17, 7.59 (each d, 2H, J = 8.0 Hz, ArH); ms: m/z (relative intensity, %) 253, 251 (M^+, 23, 24), 158 (100).

Anal. Calcd. for $C_{11}H_{10}NOBr$: C, 52.40; H, 4.00; N, 5.55. Found: C, 52.70; H, 4.12; N, 5.51.

5-Bromomethyl-3-(*p*-bromomethylphenyl)isoxazole **2**.

After a solution of **1** (8.0 g, 31.7 mmoles), *N*-bromosuccinimide (6.21 g, 34.9 mmoles) and V-65 [10] (0.43 g, 1.73

mmoles) in dichloromethane (200 ml) was refluxed for 9 hours, the solvent was evaporated *in vacuo*. The residue was extracted with hot carbon tetrachloride and the extract was concentrated *in vacuo* to leave colorless solid, which on recrystallization from ethanol gave 10.2 g (97%) of **2** as colorless needles.

This compound had mp 112-113°; ^{1}H-nmr (deuteriochloroform): δ 4.50 (s, 4H, C*H*$_2$), 6.60 (s, 1H, 4-*H* in isoxazole ring), 7.44, 7.73 (each d, 2H, J = 8.0 Hz, Ar*H*); ms: m/z (relative intensity, %) 333, 331, 329 (M$^+$, 6,12,6), 250 (100).

Anal. Calcd. for $C_{11}H_9NOBr_2$: C, 39.91; H, 2.71; N, 4.23. Found: C, 39.71; H, 2.80; N, 4.00.

Reaction of **2** with **3a**.

A solution of **2** (4.02 g, 12.1 mmoles) in benzene (100 ml) and a solution of **3a** (2.00 g, 11.8 mmoles) in benzene (100 ml) were added dropwise at the same rate each over 9.5 hours from a separated Hershberg funnel to a vigorously stirred refluxing mixture of sodium borohydride (0.44 g, 11.6 mmoles) and cesium hydroxide monohydrate (5.30 g, 31.5 mmoles) in degassed ethanol (4 l). After refluxing for an additional 2 hours, the solvents were removed *in vacuo*, and then the residue was extracted with dichloromethane. The extract was washed with water, dried over magnesium sulfate, and concentrated *in vacuo* to leave a residue, which on chromatography using benzene as an eluent gave **4a** (0.68 g, 17%) and **5a** (0.40 g, 10%).

1:1 Condensed-ring Compound **4a**.

This compound was obtained as colorless needles (ethanol), mp 186-187°; ^{13}C-nmr (deuteriochloroform): δ 29.9, 35.1, 37.5, 38.7 (*C*H$_2$), 106.8 (4-*C* in isoxazole ring), 126.0, 127.2, 128.2, 128.5, 129.5, 136.6, 136.8, 140.1 (benzene-ring *C*), 162.4 (3-*C* inisoxazole ring), 169.3 (5-*C* in isoxazole ring); ms: m/z (relative intensity, %) 339 (M$^+$, 100).

Anal. Calcd. for $C_{19}H_{17}NOS_2$: C, 67.23; H, 5.05; N, 4.13. Found: C, 67.40; H, 5.12; N, 3.94.

2:2 Condensed-ring Compound **5a**.

This compound was obtained as colorless needles (chloroform-benzene), mp 230-232°; ms: m/z (relative intensity, %) 678 (M$^+$, 31).

Anal. Calcd. for $C_{38}H_{34}N_2O_2S_4$: C, 67.23; H, 5.05; N, 4.13. Found: C, 67.55; H, 5.17; N, 3.98.

Reaction of **2** with **3b**.

To a mixture of sodium borohydride (0.45 g, 11.8 mmoles) and cesium hydroxide monohydrate (5.30 g, 31.5 mmoles) in degassed ethanol (4 l) at reflux were added dropwise at the same rate each over 13 hours from a separated Hershberg funnel a solution of **2** (3.90 g, 11.8 mmoles) in benzene (100 ml) and a solution of **3b** (2.00 g, 11.8 mmoles) in benzene (100 ml), and the mixture was refluxed for an additional 1 hour. The reaction mixture was worked up as described above, giving **4b** (39 mg, 1%) and **6b** (0.47 g, 12%).

1:1 Condensed-ring Compound **4b**.

This compound was obtained as colorless needles (benzene), mp 196-197°; ^{13}C-nmr (deuteriochloroform): δ 27.9, 33.1, 35.7, 36.9 (*C*H$_2$), 106.5 (4-*C* in isoxazole ring), 124.3, 125.5, 126.0, 127.7, 128.0, 128.3, 130.4, 137.3, 137.5, 138.1 (benzene-ring *C*), 162.1 (3-*C* in isoxazole ring), 167.5 (5-*C* in isoxazole ring); ms: m/z (relative intensity %) 339 (M$^+$, 37), 105 (100).

Anal. Calcd. for $C_{19}H_{17}NOS_2$: C, 67.23; H, 5.05; N, 4.13. Found: C, 67.37; H, 5.22; N, 3.95.

2:2 Condensed-ring Compound **6b**.

This compound was obtained as colorless needles (chloroform), mp 203-204°; ms m/z (relative intensity, %) 678 (M$^+$, 12), 57 (100).

Anal. Calcd. for $C_{38}H_{34}N_2O_2S_4$: C, 67.23; H, 5.05; N, 4.13. Found: C, 66.98; H, 5.25; N, 4.13.

Reaction of **2** with **3c**.

To a mixture of sodium borohydride (0.56 g, 14.7 mmoles) and cesium hydroxide monohydrate (6.70 g, 39.9 mmoles) in degassed ethanol (4 l) at reflux were added at the same rate each over 9 hours from a separated Hershberg funnel a solution of **2** (5.00 g, 15.1 mmoles) in benzene (100 ml) and a solution of **3c** (2.50 g, 14.7 mmoles) in benzene (100 ml), and the resultant mixture was refluxed for an additional 2 hours. The reaction mixture was concentrated *in vacuo* to leave residue, which was well washed with dichloromethane. The insoluble solid was washed with water, and recrystallized from nitrobenzene to give **6c** (2.57 g, 52%) as colorless needles.

The dichloromethane extract was concentrated *in vacuo* to leave solid which on recrystallization from nitrobenzene gave **5c** (1.07 g, 21%) as colorless needles.

2:2 Condensed-ring Compound **5c**.

This compound had mp 235-236°; ^{1}H-nmr (DMSO-d$_6$): δ 3.62, 3.64, 3.87, 3.93 (each 4H, s, C*H*$_2$), 6.75 (2H, s, 4-*H* in isoxazole ring), 7.17-7.38 (12H, m, Ar*H*), 7.73 (4H, d, J = 8.3 Hz, Ar*H*); ^{13}C-nmr (DMSO-d$_6$, 80°): δ 26.6, 33.0, 33.3, 36.3 (*C*H$_2$), 100.8 (4-*C* in isoxazole ring), 126.6, 127.3, 127.3, 127.6, 129.3, 130.1, 130.2, 135.7, 136.0, 140.4 (benzene-ring *C*), 161.7 (3-*C* in isoxazole ring), 170.2 (5-*C* in isoxazole ring); ms: m/z (relative intensity, %) 678 (M$^+$, 5), 194 (100).

Anal. Calcd. for $C_{38}H_{34}N_2O_2S_4$: C, 67.23; H, 5.05; N, 4.13. Found: C, 67.16; H, 5.05; N, 3.89.

2:2 Condensed-ring Compound **6c**.

This compound had mp 251-252°; ^{1}H-nmr (DMSO-d$_6$): δ 3.72, 3.74, 3.78, 3.83 (each 4H, s, C*H*$_2$), 6.76 (2H, s, 4-*H* in isoxazole ring), 7.18-7.40 (12H, m, Ar*H*), 7.69 (4H, d, J = 8.2 Hz, Ar*H*); ms: m/z (relative intensity, %) 678 (M$^+$, 82), 134 (100).

Anal. Calcd. for $C_{38}H_{34}N_2O_2S_4$: C, 67.23; H, 5.05; N, 4.13. Found: C, 67.33; H, 4.97; N, 4.02.

5-Mercaptomethyl-3-(*p*-mercaptomethylphenyl)isoxazole **7**.

A solution of **2** (3.0 g, 9.1 mmoles) in dimethyl sulfoxide (30 ml) was stirred with thiourea (1.5 g, 19.7 mmoles) at room temperature for 2 days under nitrogen. After the reaction mixture was poured into an ice-cooled 3% aqueous sodium hydroxide solution (100 ml), and the resultant mixture was stirred for 2 hours at room temperature, the mixture was acidified with a 10% hydrochloric acid, and then extracted with dichloromethane. The extract was washed with water, dried over magnesium sulfate, and concentrated *in vacuo* to give 1.8 g (84%) of **7**.

Compound **7** was obtained as colorless prisms (*n*-hexane), mp 76-77°; ^{13}C-nmr (deuteriochloroform): δ 19.2, 28.7 (*C*H$_2$), 99.9 (4-*C* in isoxazole ring), 127.1, 127.6, 128.6, 143.2 (benzene-ring *C*), 162.2 (3-*C* in isoxazole ring), 171.8 (5-*C* in isoxazole ring); ms: m/z (relative intensity, %) 237 (M$^+$, 48), 204 (100).

Anal. Calcd. for $C_{11}H_{11}NOS_2$: C, 55.69; H, 4.67; N, 5.91. Found: C, 55.73; H, 4.85; N, 5.68.

Reaction of **2** with **7**.

To a vigorously stirred refluxing solution of sodium borohydride (0.12 g, 3.2 mmoles) and cesium hydroxide monohydrate (2.40 g, 14.3 mmoles) in degassed ethanol (4 l), a solution of **2** (1.90 g, 5.7 mmoles) in benzene (100 ml) and a solution of **7** (1.30 g, 5.5 mmoles) in benzene (100 ml) were added dropwise at the same rate each from a separated hershberg funnel over a 10-hour period, and then the reaction mixture was refluxed for an additional 2 hours. The solvent from the mixture was removed *in vacuo*, and the residue was extracted with dichloromethane. The extract was washed with water, dried over magnesium sulfate, concentrated *in vacuo*, and then chromatographed on silica gel using chloroform as an eluent to afford 1.05 g (47%) of a mixture of two 1:1 condensed-ring compounds **8** and **9**.

The mixture of **8** and **9** was obtained as colorless prisms (nitrobenzene), mp 290-293°; ^{1}H-nmr (DMSO-d_6, 150°): δ 3.86 (1.2H, s, CH_2 of **9**), 3.91 (5.6H, s, CH_2 of **8**), 4.05 (1.2H, s, CH_2 of **9**), 5.48 (1.4H, s, 4-*H* in isoxazole ring of **8**), 6.17 (0.6H, s, 4-*H* in isoxazole ring of **9**), 7.00, 7.14 (each 1.2H, d, J = 8.3 Hz, Ar*H* of **9**), 7.18, 7.24 (each 2.8H, d, J = 8.2 Hz, Ar*H* of **8**); ms: m/z (relative intensity, %) 406 (M^+, 100).

Anal. Calcd. for $C_{22}H_{18}N_2O_2S_2$: C, 65.02; H, 4.43; N, 6.68. Found: C, 65.30; H, 4.50; N, 6.48.

REFERENCES AND NOTES

[1] W. W. Paudler and M. D. Bezoari, in Cyclophanes, Vol **2**, P. M. Keehn and S. M. Rosenfeld, eds, Academic Press, New York, 1983, pp 359-441.

[2] A. P. Kozikowski, in Comprehensive Heterocyclic Chemistry, Vol **1**, A. R. Katritzky and C. W. Rees, eds, Pergamon Press, Oxford, 1984, pp 413-491.

[3] D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1986).

[4] T. Hatta, S. Mataka, and M. Tashiro, *J. Heterocyclic Chem.*, **23**, 813 (1986).

[5] S. Albanesi, A. Harchesini, and B. Gioia, *Tetrahedron Letters*, 1875 (1979); E. M. Beccalli, L. Majori, A. Marchesini, and C. Torricelli, *Chem. Letters*, 659 (1980); S. Auricchio, A. Ricca, and O. V. de Para, *J. Heterocyclic Chem.*, **18**, 1471 (1981); S. H. Mashraqui and P. M. Keehn, *J. Org. Chem.*, **48**, 1341 (1983); I. Heinze and W. Eberbach, *Tetrahedron Letters*, 2051 (1988).

[6] T. Hatta, S. Mataka, M. Tashiro, K. Mumano, S. Tanimoto, and A. Tori-i, *J. Heterocyclic Chem.*, **27**, 1861 (1990).

[7] T. Hatta, S. Mataka, S. Tanimoto, M. Tashiro, and O. Tsuge, *Bull. Chem. Soc. Japan*, **65**, 1469 (1992).

[8] W. Brugel, Handbook of NMR Spectral Parameters, Vol **1**, Heyden and Son Ltd., London, 1979, p 44.

[9] W. Brugel, Handbook of NMR Spectral Parameters, Vol **1**, Heyden and Son Ltd., London, p 42.

[10] Commercial name (Wako Pure Chemical Industries Ltd.) of 2,2'-azobis(2,4-dimethylvaleronitrile).