Syntheses of 9-Phenylsufonylimino-1,4-dioxa-8,10-diazacyclotridecanes and 9,22-Bis(phenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosanes: Macrocyclization via Dimethyl *N*-Phenylsulfonylcarbonimidodithioates

Naoaki FUKADA,* Minoru TAKANO, Kazutaka NAKAI, Satoshi KUBOIKE, and Yasuyuki TAKEDA
Department of Chemistry, Faculty of Science, Chiba University, Yayoicho, Inage-ku, Chiba 263
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The reaction of dimethyl *N*-phenylsulfonylcarbonimidodithioates (**1**) with diamines gave three different types of products due to changes in the molar ratio of the starting materials. From aliphatic diamines heterocyclic 1:1 and acyclic 2:1 reaction products were obtained. In order to prepare macrocycles, the reaction of **1** with 1,10-diamino-4,7-dioxadecane (**10**) was carried out. 1,1′-(4,7-Dioxadecamethylene)bis(2-methyl-3-phenylsulfonylisothiourea)s (**11**) and 9-phenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecanes were obtained by 2:1- and 1:2-mixed reactions of **1** with **10**, respectively. The 2:2 reaction products, 9,22-bis(phenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosanes, were prepared from **1** and a greater excess of diamine **10** (1:4) or from **11** and diamine **10**.

Dimethyl *N*-phenylsulfonylcarbonimidodithioates (**1**) are used as starting materials for the synthesis of various heterocyclic compounds,[1—8] even though they are not very well known in the literature as α-oxo ketene dithioacetals. The reaction of dithioate **1**, as well as α-oxo ketene dithioacetals[9,10] and dimethyl *N*-benzoylcarbonimidodithioates,[11—17] with amines by mono- or di-substitution of two methylthio groups gives isothiourea or guanidine derivatives.

Rodricks and Rapoport[3] have reported that dimethyl *N*-tosylcarbonimidodithioate (**1b**) reacts with a variety of aliphatic and aromatic diamines in aqueous ethanol under reflux to give easily isolable tosyl-protected cyclic guanidines. They also obtained, in addition to the guanidines, polymeric side products from **1b** and aliphatic diamines; no compounds of high molecular weight were obtained from ethylenediamine (**2**), 16% from 1,4-diaminobutane (**3**), and 100% from 1,6-diaminohexane (**4**). Indeed, we obtained imidazoline and diazepine derivatives **5** and **6** by reacting the corresponding **1** and diamines **2** and **3** in ethanol under reflux; no 9-membered ring compounds were obtained from **1** and **4**. However, our reaction of dithioate **1** with **3** under reflux for 20 h afforded 2:1 reaction products **8** in addition to cyclic guanidines **6**. In this case we found that a greater excess of diamine **3** reduced the formation of compounds **8** (Table 1).

For the purpose of obtaining only 2:1 reaction products, the ratio of the starting materials **1** and diamines **2**—**4** was set at 2:1. The reaction under reflux for 20 h or at room temperature for 40 h led to good yields of 1,1′-di-, 1,1′-tetra-, and 1,1′-hexamethylenebis(2-methyl-3-phenylsulfonylisothiourea)s (**7**—**9**). However, in the case of diamine **2**, especially at room temperature, the yields of compounds **7a**—**c** decreased, probably due to the ease of formation of 5-membered ring compounds **5** (Table 2) (Scheme 1).

In order to prepare macrocycles, the reaction of dithioate **1** with 1,10-diamino-4,7-dioxadecane (**10**) was carried out on the basis of the observation described above. First, acyclic 2:1 reaction products, 1,1′-(4,7-dioxadecamethylene)bis(2-methyl-3-phenylsulfonylisothiourea)s (**11**), were easily obtained from the reaction using double the molar quantity of dithioate **1** for diamine **10**. The yields by the reaction at room temperature were rather higher than under reflux. In the case of **1d**, compound **11d** could not be isolated from the reaction under reflux (Table 3).

The synthesis of 13-membered macrocyclic 1:1 reaction products **12**, was conducted first using equimolecular quantities of dithioate **1** and diamine **10**. The reaction under reflux condition afforded the expected compounds, 9-phenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecanes (**12**), in low yields. We found that using double the molar quantity of **10** resulted in much higher yields of **12**. However, from the reaction of **1e** with **10**, the compound corresponding to **12e** could not be iso-

Table 1. 2-Phenylsulfonylamino-2-imidazolines (**5**) and 2-Phenylsulfonylamino-4,5,6,7-tetrahydro-1,3-diazepines (**6**)

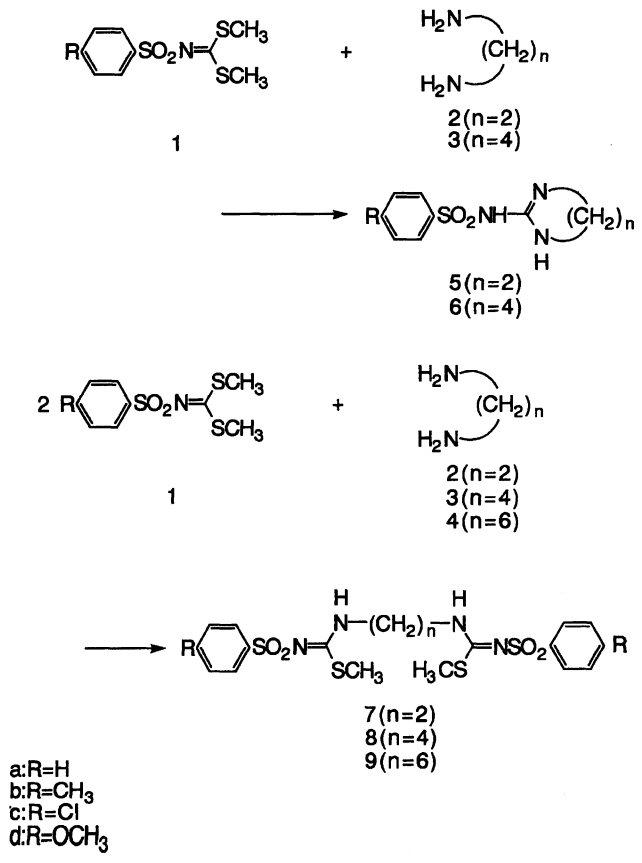
Compd	R	*n*	Yield [a] %	Mp θ_m/°C (Solvent)
5b	CH_3	2	80	228—230 [b] (MeOH)
5c	Cl	2	78	211—212 (EtOH)
5d	OCH_3	2	83	198—200 (DMF)
6b	CH_3	4	49 (18)	216—218 [c] (Me_2CO)
6c	Cl	4	35 (39) 45[d] (26) 48[e] (19) 46[f] (14)	184—186 (EtOH)

a) The yield is given for the 1:1-mixed reaction of **1** with **2** or **3**. The yield in parenthesis refers to that of by-product **8**, based on **1**. b) Lit, [1] 232°C. c) Lit, [3] 221—233°C. d) By the 1:2-mixed reaction of **1c** with **3**. e) By the 1:4-mixed reaction. f) By the 1:8-mixed reaction.

Table 2. 1,1′-Polymethylenebis(2-methyl-3-phenylsulfonylisothiourea)s (**7**—**9**)

Compd	R	n	Yield[a] (%) R.T.	Yield[a] (%) Reflux	Mp θ_m/°C (Solvent)
7a	H	2	42	65	158—160 (CH_2Cl_2)
7b	CH_3	2	34	60	199—202 (DMF)
7c	Cl	2	45	62	212—214 (DMF)
8b	CH_3	4	82	91	222—224 (DMF–H_2O)
8c	Cl	4	87	96	214—216 (DMF–H_2O)
9b	CH_3	6	93	95	138—140 (EtOH–$CHCl_3$)
9c	Cl	6	86	98	172—174 (DMF)

a) The yield is given for the 2 : 1-mixed reaction of **1** with **2**, **3**, or **4** at room temperature or under reflux.



Scheme 1.

lated; the 1 : 1-mixed reaction of **1e** with **10** led to compound **11e**, and the 1 : 2-mixed one to the 2 : 2 reaction product **13e** described below (Table 4) (Scheme 2).

We recently reported on a similar synthesis of macrocyclic compounds by a reaction of dimethyl *N*-benzoylcarbonimidodithioates and diamine **10** or 1,13-diamino-4,7,10-trioxatridecane under high-dilution conditions.[17] Although the yields of ten macrocycles from the reaction using equimolecular quantities of the starting material, benzamide derivatives and polyether-containing diamines, covered 16 to 80%, they might increase if an excess of the diamines was used.

Table 3. 1,1′-(4,7-Dioxadecamethylene) bis(2-methyl-3-phenylsulfonylisothiourea)s (**11**)

Compd	R	Yield[a] (%) R.T.	Yield[a] (%) Reflux	Mp θ_m/°C (Solvent)
11a	H	84	51	92—94 (EtOH)
11b	CH_3	92	92	99—100 (EtOH)
11c	Cl	97	93	109—111 (EtOH)
11d	OCH_3	82	—	93—94 (EtOH)
11e	NH_2	94	91	162—163 (EtOH–H_2O)

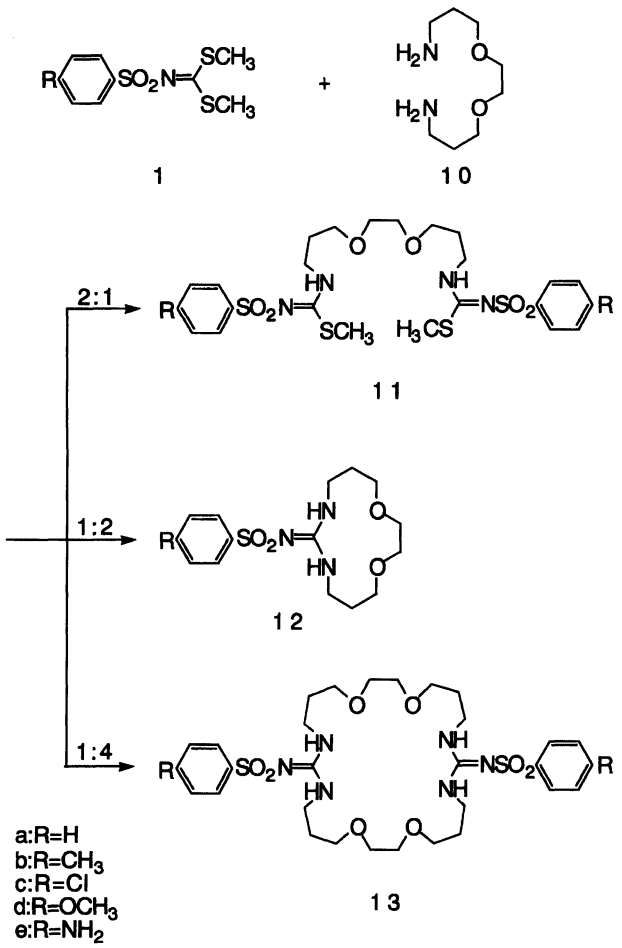
a) The yield is given for the 2 : 1-mixed reaction of **1** with **10** at room temperature or under reflux.

Table 4. 9-Phenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecanes (**12**)

Compd	R	Yield[a] (%) 1 : 1	1 : 2	1 : 3	Mp θ_m/°C (Solvent)
12a	H	11	81	73	109—111 (EtOH)
12b	CH_3	10	87	19	121—122 (EtOH)
12c	Cl	38	67	28	110—112 (EtOH)
12d	OCH_3	22	83	58	122—124 (EtOH)

a) The yield is given for the 1 : 1-, 1 : 2-, or 1 : 3-mixed reaction of **1** with **10**.

Some reactions of dithioate **1** with a greater excess of diamine **10** were carried out. By the 1 : 4-mixed reaction, 26-membered ring 2 : 2 reaction products, 9,22-bis(phenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosanes, **13b**, **13c**, and **13e**, were obtained in low yields. It is known that in some cases 2 : 2 reaction products are formed by reactions leading to macrocyclic compounds. For example, the reaction of disodium 2-thioxo-1,3-dithiole-4,5-dithiolate with 1,8-dibromo-3,6-dioxaoctane gives the 2 : 2 macrocycle as the main product, along with a small amount of the 1 : 1 macrocycle.[18] In the case of **1a**, the reaction afforded 70% of compound **12a**; even a 1 : 8-mixed reaction gave 30% of **12a**. From the reaction mixture of **1d** and **10**, compound **12d** was obtained in 20% yield. The reaction mechanism leading directly to **13** may involve an intermediate **14** (Chart 1), rather than compound **11**. Due to the fact that the 2 : 1- and 1 : 2-mixed reactions of **1** with **10** afforded **11** and **12**, respectively, in good yields, it is rather difficult to assume the formation of the intermediate **11** in the presence of a greater excess



Scheme 2.

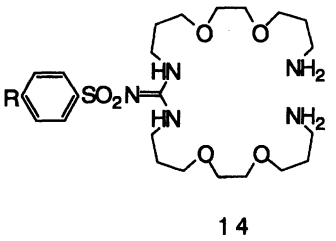


Chart 1.

of the diamine. However, attempts to isolate compound **14** were unsuccessful. On the other hand, the 2:2 reaction products **13a**—**e** were prepared by the reaction of intermediates **11a**—**e** with **10** in moderate to good yields(Table 5).

All of the new compounds were characterized by microanalysis as well as by spectral data. The structure of the small and inflexible ring compounds **5** and **6**, at least in the crystalline state, may involve the endocyclic C,N double bond, as suggested by Gompper[2] and Rapoport;[3] their IR spectra show two single NH stretching band in the 3360—3100 cm^{-1} region. On the other hand, the IR spectra of the acyclic and more flexible compounds **7**—**9** and **11**, as well as macrocyclic compounds **12** and **13** show only a single NH band, which indicates either $-SO_2N=$ or the exocyclic C,N double bond structure. Also, in the ^1H NMR spectrum of **9b** in $CDCl_3$ a decoupling study by each irradiation to methylenes supports the $-NHCH_2-$ structure. The EI mass spectra of **12** showed molecular-ion peaks for the 1:1 reaction product, with no additional peaks above them. Although the EI mass spectra of **11** and **13** showed no molecular-ion peaks, their FAB mass spectra (matrix: 3-nitrobenzyl alcohol) showed $(M+H)^+$ peaks.

The reactivities of dithioate **1** for amines seemed to be almost similar to those of the α-oxo ketene dithioacetals[9,10] and dimethyl *N*-benzoylcarbonimidodithioates.[11—17] We examined only the main products of all the reactions, and did not further investigate the residue of complex reaction mixtures. It is convenient that the progress as well as the termination of all of the reactions described above can be judged by detecting the odor of methanethiol. Studies concerning the metal-ion binding properties of macrocycles **12** and **13** are in progress.

Experimental

Dimethyl *N*-Phenylsulfonylcarbonimidodithioates (1) were prepared by the reaction of dipotassium salts[19] of the corresponding *N*-phyenylsulfonylcarbonimidodithioic acid with methyl iodide in water at room temperature.

2-*p*-Chlorophenylsulfonylamino-2-imidazoline (5c). A mixture of dithioate **1c** (0.59 g, 0.002 mol), ethylenediamine (**2**) (0.12 g, 0.002 mol), and ethanol (20 ml) was refluxed using a cotton wool-topped reflux condenser under a fume hood until the odor of methanethiol could no longer be detected (20 h). The mixture was kept for several days at −20°C. The solid which precipitated was collected and recrystallized: IR (KBr) 3360vs, 3100vs, and 1608vs cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.65 (s, 4H, CH_2), 6.62 (s, 2H, NH), 7.41 (d, 2H, arom. 3′,5′-H), and 7.80 (d, 2H, arom. 2′,6′ -H). Found: C, 41.65; H, 3.96; N, 16.08%. Calcd for $C_9H_{10}N_3O_2SCl$: C, 41.62; H, 3.88; N, 16.18%.

2- *p*- Methoxyphenylsulfonylamino- 2- imidazoline (5d) was prepared by the method used for **5c**: IR (KBr) 3350s, 3100vs, and 1590vs cm^{-1}. Found: C, 46.95; H, 5.15; N, 16.29%. Calcd for $C_{10}H_{13}N_3O_3S$: C, 47.05; H, 5.13; N, 16.46%.

2- *p*- Chlorophenylsulfonylamino- 4, 5, 6, 7- tetrahydro-1,3-diazepine (6c). A mixture of dithioate **1c** (0.59 g, 0.002 mol), 1,4-diaminobutane (**3**) (0.18 g, 0.002 mol), and ethanol (20 ml) was refluxed for 20 h. Without cooling the mixture, compound **8c** (described below) (yield 39%) which precipitated was filtered off. The filtrate was worked up as described for **5c**: Yield 35%; IR (KBr) 3300s, 3200vs, and 1590vs cm^{-1}. Found: C, 45.65; H, 4.88; N, 14.41%. Calcd for $C_{11}H_{14}N_3O_2SCl$: C, 45.91; H, 4.90;N, 14.60%.

The yields of **6c** and **8c** by the 1:2-, 1:4, or 1:8-mixed reaction of **1** with **3** are shown in Table 1.

1,1′-Polymethylenebis(2-methyl-3-phenylsulfonylisothiourea)s (7—9). General Procedure. A mixture of dithioate **1** (0.002 mol), diamine **2**, **3**, or **4** (0.001 mol), and ethanol (20 ml) was either refluxed for 20 h, or was stirred for 40 h at room temperature until no methanethiol odor evolved. The reaction mixture was cooled to room temperature; the solid which precipitated was collected, washed with ethanol, and recrystallized.

Table 5. 9,22-Bis(phenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosanes (**13**)

Compd	R	Yield[a] (%) From **1**	Yield[a] (%) From **11**	Mp θ_m/°C (Solvent)
13a	H	—[b]	70	138—140 (EtOH)
13b	CH_3	32	94	173—174 (EtOH)
13c	Cl	26	90	172—173 (EtOH)
13d	OCH_3	—[c]	67	150—151 (CH_2Cl_2–EtOH)
13e	NH_2	12	57	208—210 (Py–H_2O)

a) The yield is given for the 1 : 4-mixed reaction of **1** with **10** or for the 1 : 2-mixed reaction of **11** with **10**. b) The reaction gave **12a** in 70% yield. c) The reaction gave **12d** in 20% yield.

1,1′-Ethylenebis(2-methyl-3-phenylsulfonylisothiourea) (7a): IR (KBr) 3310vs and 1590s cm^{-1}. Found: C, 44.70; H, 4.65; N, 11.71%. Calcd for $C_{18}H_{22}N_4O_4S_4$: C, 44.43; H, 4.56; N, 11.51%.

1,1′-Ethylenebis(2-methyl-3-*p*-tolylsulfonylisothiourea) (7b): IR (KBr) 3325vs and 1610s cm^{-1}. Found: C, 46.66; H, 5.28; N, 10.95%. Calcd for $C_{20}H_{26}N_4O_4S_4$: C, 46.67; H, 5.09; N, 10.89%.

1,1′-Ethylenebis(3-*p*-chlorophenylsulfonyl-2-methylisothiourea) (7c): IR (KBr) 3340vs and 1615vs cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=2.42 (s, 6H, SCH_3), 3.45 (m, 4H, NCH_2), 7.58 (m, 4H, arom. 3′,5′-H), 7.79 (m, 4H, arom. 2′,6′-H), and 8.11 (br s, 2H, NH). Found: C, 39.14; H, 3.71; N, 10.39%. Calcd for $C_{18}H_{20}N_4O_4S_4Cl_2$: C, 38.92; H, 3.63; N, 10.09%.

1,1′-Tetramethylenebis(2-methyl-3-*p*-tolylsulfonylisothiourea) (8b): IR (KBr) 3325vs and 1525vs cm^{-1}. Found: C, 48.82; H, 5.80; N, 10.56%. Calcd for $C_{22}H_{30}N_4O_4S_4$: C, 48.68; H, 5.57; N, 10.32%.

1,1′-Tetramethylenebis(3-*p*-chlorophenylsulfonyl-2-methylisothiourea) (8c): IR (KBr) 3325vs and 1520vs cm^{-1}. Found: C, 41.38; H, 4.36; N, 9.67%. Calcd for $C_{20}H_{24}N_4O_4S_4Cl_2$: C, 41.16; H, 4.15; N, 9.60%.

1,1′-Hexamethylenebis(2-methyl-3-*p*-tolylsulfonylisothiourea) (9b): IR (KBr) 3330vs and 1520vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.36 (m, 4H, CH_2), 1.61 (m, 4H, CH_2), 2.37 (s, 6H, SCH_3), 2.41 (s, 6H, arom. 4′-CH_3), 3.27 (quart, 4H, NCH_2), 7.27 (d, 4H, arom. 3′,5′-H), 7.79 (d, 4H, arom. 2′,6′-H), and 8.19 (br s, 2H, NH). Found: C, 50.30; H, 6.03; N, 9.70%. Calcd for $C_{24}H_{34}N_4O_4S_4$: 50.50; H, 6.00; N, 9.82%.

1,1′-Hexamethylenebis(3-*p*-chlorophenylsulfonyl-2-methylisothiourea) (9c): IR (KBr) 3340vs and 1530vs cm^{-1}. Found: C, 43.26; H, 4.68; N, 9.37%. Calcd for $C_{22}H_{28}N_4O_4S_4Cl_2$: C, 43.20; H, 4.61; N, 9.16%.

1,1′-(4,7-Dioxadecamethylene)bis(2-methyl-3-phenylsulfonylisothiourea)s (11). General Procedure. A mixture of dithioate **1** (0.008 mol), 1,10-diamino-4,7-dioxadecane (**10**) (0.71 g, 0.004 mol), and ethanol (200 ml) was either stirred for 7 d at room temperature, or was refluxed for 40 h until no methanethiol odor evolved. The solid which precipitated was collected and recrystallized.

If the reaction mixture was a clear solution (mostly refluxed solution), the solvent was evaporated, ethanol (10 ml) was added to the residual oil, and the mixture was then transferred to a refrigerator.

1,1′-(4,7-Dioxadecamethylene)bis(2-methyl-3-phenylsulfonylisothiourea) (11a): IR (KBr) 3260vs and 1570vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.86 (quint, 4H, CH_2), 2.40 (s, 6H, SCH_3), 3.42 (quart, 4H, NCH_2), 3.59 (t, 4H, OCH_2), 3.68 (s, 4H, OCH_2CH_2O), 7.50 (m, 6H, arom. 3′,4′,5′-H), 7.92 (m, 4H, arom. 2′,6′-H), and 8.45 (br s, 2H, NH); UV (EtOH) λ_{max} 209 (log ε 3.92) and 238 nm (4.02); FAB MS (NBA) m/z 603 (89%) $(M+H)^+$. Found: C, 47.96; H, 5.70; N, 9.43%. Calcd for $C_{24}H_{34}N_4O_6S_4$: C, 47.82; H, 5.69; N, 9.29%.

1,1′-(4,7-Dioxadecamethylene)bis(2-methyl-3-*p*-tolylsulfonylisothiourea) (11b): IR (KBr) 3270vs and 1540vs cm^{-1}; UV (EtOH) λ_{max} 205 (log ε 4.10) and 240nm (4.17). Found: C, 49.57; H, 6.09; N, 8.80%. Calcd for $C_{26}H_{38}N_4O_6S_4$: C, 49.50; H, 6.07; N, 8.88%.

1,1′-(4,7-Dioxadecamethylene)bis(3-*p*-chlorophenylsulfonyl-2-methylisothiourea) (11c): IR (KBr) 3265vs and 1575vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.86 (quint, 4H, CH_2), 2.35 (s, 6H, SCH_3), 3.42 (quart, 4H, NCH_2), 3.61 (t, 4H, OCH_2), 3.70 (s, 4H, OCH_2CH_2O), 7.44 (d, 4H, arom. 3′,5′-H), 7.86 (d, 4H, arom. 2′,6′-H), and 8.46 (br s, 2H, NH); UV (EtOH) λ_{max} 205 (log ε 4.39), 225sh (4.44), and 240 nm (4.52); FAB MS (NBA) m/z 671(100%), 673 (86%) $(M+H)^+$. Found: C, 42.91; H, 4.81; N, 8.34%. Calcd for $C_{24}H_{32}N_4O_6S_4Cl_2$: C, 42.92; H, 4.80; N, 8.34%.

1,1′-(4,7-Dioxadecamethylene)bis(3-*p*-methoxyphenylsulfonyl-2-methylisothiourea) (11d): IR (KBr) 3370vs and 1595vs cm^{-1}; UV (EtOH) λ_{max} 204 (log ε 4.29), 228 (4.20), and 249 nm (4.30). Found: C, 46.86; H, 5.93; N, 8.17%. Calcd for $C_{26}H_{38}N_4O_8S_4$: C, 47.11; H, 5.78; N, 8.45%.

1,1′-(4,7-Dioxadecamethylene)bis(3-*p*-aminophenylsulfonyl-2-methylisothiourea) (11e): IR (KBr) 3435s, 3340vs, 3300s, 3235s, 1630s, and 1590vs cm^{-1}. Found: C, 45.37; H, 5.76; N, 13.03%. Calcd for $C_{24}H_{36}N_6O_6S_4$: C, 45.55; H, 5.73; N, 13.28%.

9-Phenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecanes (12). General Procedure. A mixture of dithioate **1** (0.004 mol), diamine **10** (1.41 g, 0.008 mol), and ethanol (200 ml) was refluxed using a cotton wool-topped reflux condenser under a fume hood until the methanethiol odor could no longer be detected (40 h). The solvent was evaporated, ethanol (10 ml) was added to the residual oil, and the mixture was kept for 7 d at −20°C.

9-Phenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecane (12a): IR (KBr) 3290vs and 1595vs cm^{-1}: ^{1}H NMR ($CDCl_3$) δ=1.80 (quint, 4H, CH_2), 3.20—3.90 (m, 8H, NCH_2 and OCH_2), 3.57 (s, 4H, OCH_2CH_2O), 6.80 (br s, 2H, NH), 7.43 (m, 3H, arom. 3′,4′,5′-H), and 7.90 (m, 2H, arom. 2′,6′-H); UV (EtOH) λ_{max} 205 (log ε 4.03) and 224sh nm (3.76); MS m/z 341 (M^+). Found: C, 52.54; H, 6.74; N, 12.15%. Calcd for $C_{15}H_{23}N_3O_4S$: C, 52.77; H, 6.79; N, 12.31%.

9-*p*-Tolylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecane (12b): IR (KBr) 3320vs and 1585vs cm^{-1}; UV (EtOH) λ_{max} 205 (log ε 4.00) and 232 nm (3.81); MS m/z 355 (M^+). Found: C, 53.80; H, 7.04; N, 11.56%. Calcd

for $C_{16}H_{25}N_3O_4S$: C, 54.06; H, 7.09; N, 11.82%.

9-*p*-Chlorophenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecane (12c); IR (KBr) 3300vs and 1590vs cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77 (quint, 4H, CH_2), 3.28—3.70 (m, 8H, NCH_2 and OCH_2), 3.58 (s, 4H, OCH_2CH_2O), 6.58 (br s, 2H, NH), 7.40 (m, 2H, arom. 3′,5′-H), and 7.82 (m, 2H, arom. 2′,6′-H); UV (EtOH) λ_{max} 205 (log ε 4.03) and 235 nm (3.84); MS *m/z* 375 (M^+). Found: C, 47.85; H, 5.88: N, 11.08%. Calcd for $C_{15}H_{22}N_3O_4SCl$: C, 47.93; H, 5.90; N, 11.18%.

9-*p*-Methoxyphenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecane (12d): IR (KBr) 3325vs and 1580vs cm^{-1}; UV (EtOH) λ_{max} 206 (log ε 4.15) and 241 nm (4.07); MS *m/z* 371 (M^+). Found: C, 51.55; H, 6.78; N, 11.08%. Calcd for $C_{16}H_{25}N_3O_5S$: C, 51.74; H, 6.78; N, 11.31%

9,22-Bis(phenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosanes (13). General Procedure. (A) From Dithioate 1. A mixture of dithioate **1** (0.004 mol), diamine **10** (2.82 g, 0.016 mol), and ethanol (200 ml) was refluxed for 40 h, and worked up as described for **12**. In the cases of **1a** and **1d**, the reaction afforded 1:1 reaction products, **12a** (yield 70%) and **12d** (20%), respectively.

(B) From Intermediate 11. A mixture of compound **11** (0.001 mol), diamine **10** (0.35 g, 0.002 mol), and ethanol (100 ml) was refluxed for 40 h, and worked up as described for **12**.

9,22-Bis(phenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosane (13a): IR (KBr) 3280vs and 1560vs cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.76 (quint, 8H, CH_2), 3.30 (m, 8H, NCH_2), 3.49 (t, 8H, OCH_2), 3.54 (s, 8H, OCH_2CH_2O), 6.70 (br s, 4H, NH), 7.45 (m, 6H, arom. 3′,4′,5′-H), and 7.87 (m, 4H, arom. 2′,6′-H); FAB MS (NBA) *m/z* 683 (100%) $(M+H)^+$. Found: C, 52.62; H, 6.86; N, 12.08%. Calcd for $C_{30}H_{46}N_6O_8S_2$: C, 52.77; H, 6.79; N, 12.31%.

9,22-Bis(*p*-tolylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosane (13b): IR (KBr) 3280vs and 1545vs cm^{-1}. Found: C, 53.72; H, 7.09; N, 11.59%. Calcd for $C_{32}H_{50}N_6O_8S_2$: C, 54.06; H, 7.09; N, 11.82%.

9,22-Bis(*p*-chlorophenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosane (13c): IR (KBr) 3310vs and 1575vs cm^{-1}; ^1H NMR ($CDCl_3$) δ= 1.78 (m, 8H, CH_2), 3.29 (m, 8H, NCH_2), 3.51 (m, 8H, OCH_2), 3.56 (s, 8H, OCH_2CH_2O), 6.20 (br s, 4H, NH), 7.39 (d, 4H, arom. 3′,5′-H), and 7.82 (d, 4H, arom. 2′,6′-H); FAB MS (NBA) *m/z* 751 (50%), 753 (37%) $(M+H)^+$. Found: C, 47.78; H, 6.05; N, 10.90%. Calcd for $C_{30}H_{44}N_6O_8S_2Cl_2$: C, 47.93; H, 5.90; N, 11.18%.

9,22-Bis(*p*-methoxyphenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosane (13d): IR (KBr) 3300vs and 1570vs cm^{-1}. Found: C, 51.59; H, 6.83; N, 11.09%. Calcd for $C_{32}H_{50}N_6O_{10}S_2$: C, 51.74; H, 6.78; N, 11.31%.

9,22-Bis(*p*-aminophenylsulfonylimino)-1,4,14,17-tetraoxa-8,10,21,23-tetraazacyclohexacosane (13e): IR (KBr) 3450s, 3420s, 3340vs, and 1580vs cm^{-1}. Found: C, 50.12; H, 6.87; N, 15.58%. Calcd for $C_{30}H_{48}N_8O_8S_2$: C, 50.54; H, 6.79; N, 15.72%.

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