Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Sulfur-Containing Macroheterocycles

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To cite this Article Voronkov, Mikhail G. and Knutov, Vladimir I.(1986) 'Sulfur-Containing Macroheterocycles', Journal of Sulfur Chemistry, 6: 3, 137 — 249
To link to this Article: DOI: 10.1080/01961778608082497
URL: http://dx.doi.org/10.1080/01961778608082497

Sulfur Reports
Volume 6(3), August 1986, pp. 137–256

Printed in the United Kingdom

SULFUR-CONTAINING MACROHETEROCYCLES

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(Received July 2, 1985)

Synthetic methods for, and structural and spectroscopic characteristics of sulfur-containing macroheterocycles are discussed. The synthesis of oligothiamacrocycloalkanes is based on the reaction of α,ω-dihaloalkanes with alkali α,ω-alkanedithiolates to form 12-42-membered macroheterocycles with 2-6 sulfur atoms in the ring. Oxathiamacrocycloalkanes containing sulfur and oxygen atoms in the ring have been prepared by reaction of aromatic 1,2-dithiols or 2-mercaptophenols with aliphatic α-ω-dihalo derivatives. The synthesis of thiamacrocycloalkanes involves the reaction of dimethyl ethers or α,ω-alkanedicarboxylic acid dichlorides with α,ω-alkanediamines followed by reduction of the macroheterocyclic diamides with $LiAlH_4$ or B_2H_6. Oxathiaazamacrocycloalkanes have been prepared in a similar way by reaction of dicarboxylic acid dichlorides with α,ω-oxaalkanediamines as well as by reaction of chlorosulfonyl-β-lactams with glycols.

A general synthetic route to oligothiacyclophanes is the reaction of bis-(bromomethyl) substituted arenes with bis-(mercaptomethyl)benzenes. Analogously, sulfur-containing cyclopyridinophanes have been prepared by reaction of 2,6-bis(bromomethyl)pyridine with α,ω-alkanedithiols. For the synthesis of macrocyclic compounds containing one, two, or several thiophene rings, some procedures based on intra- and intermolecular acylation of ω-thienylalkanecarboxylic acid chlorides, acyloin condensation of 2,5-bis(carbalkoxyalkyl)thiophenes, and intramolecular alkylation of ω-haloalkyl substituted β-keto esters of the thiophene series have been developed.

Synthetic routes to macroheterocycles containing di- and polysulfide groups are discussed. The synthesis involves sulfurization of mesitylene or 1,3-dimethoxybenzene with disulfur dichloride or sulfur dichloride as well as the oxidation of dithiols.

The synthesis of bi- and trimacrocyclic compounds is based on the reaction of 1,3,5-tris(mercaptoalkyl)benzenes with tris(bromoalkyl)-methanes or 1,3,5-tris[4-(mercaptomethyl)phenyl]-benzene with 1,3,5-tris- [4-(bromomethyl)phenyl] benzene.

Some methods for the synthesis of sulfur-containing macroheterocycles containing silicon, tellurium, or iron are considered.

The structures of the sulfur-containing macroheterocycles are discussed using the results of X-ray diffraction, ^1H NMR, IR, and UV spectroscopy as well as their electroconductive and magnetic properties.

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I. INTRODUCTION

The chemistry of macrocyclic compounds took its beginning more than half a century ago. It was pioneered by Ružička who synthesized macrocyclic ketones to elucidate the nature of the active principle of musk-smelling substances.[1–4] Further development of this interesting field of organic chemistry was promoted by investigations carried out by Ziegler,[5–9] Hansly,[10] Prelog,[11] Stoll,[12,13] Shemyakin,[14–16] and others[17–20] in 1930–1960.

At present the chemistry of macrocyclic compounds is developing rather vigorously. This is due to the wide possibilities found recently of the application of macrocyclic compounds in not only organic synthesis, but in biology, medicine, and engineering as well.[21–23] Much attention has been drawn to the synthesis of catenanes and rotaxanes, crown ethers and cryptands, cyclophanes, ansa compounds, annulenes, etc. Natural macroheterocyclic compounds are of concern as well. Investigations of natural macroheterocycles such as peptides, depsipeptides, and depsides have re-

vealed the ability of these compounds to form stable complexes with alkali and alkali earth metal ions and to transport these cations through artificial and biological membranes. Such compounds are called membrano-active complexones or ionophores.[21] The development of the chemistry of synthetic macroheterocyclic complexones is related to the possibility of preparing compounds analogous to natural macroheterocycles, which may be regarded as simplified models of natural macroheterocyclic ionophores. Some synthetic macroheterocyclic complexones have been obtained by different groups of scientists.[24–29] However, more intensive studies have been stimulated by work of Pedersen dealing with the synthesis and investigation of the complexation of macroheterocyclic polyethers with salts of alkali and alkali earth metals.[30] Recent monographs[21–23,31,32] and reviews, both general[33] and dedicated to certain classes of macroheterocycles such as ethers,[34] esters,[35] amines,[36] sulfides,[37,38] heterocyclophanes,[39] and others,[40–43] have provided strong evidence for the vigorous development of the chemistry of macroheterocycles. Among all the above compounds the macroheterocyclic systems containing sulfur heteroatoms in the heteroring are of special interest. Of two reviews[37,38] concerning these compounds, one is out of date and the other is in Russian and hardly accessible to the English-speaking reader.

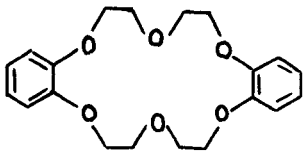
The present review summarizes as exhaustively as possible the literature concerning sulfur-containing macroheterocyclic compounds through 1983.

II. SYNTHESIS OF SULFUR-CONTAINING MACROHETEROCYCLES

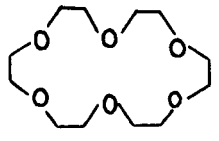
1. Monocyclic Systems

1.1. Oligothiamacrocycloalkanes

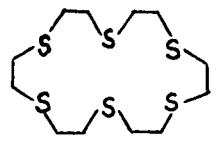
In 1967 Pedersen synthesized aromatic macroheterocyclic polyethers of type *1* and named them crown ethers.[30] He also found that these compounds form stable complexes with cations of alkali and alkali earth metals, ammonium, and silver. Crown ethers are prepared by reaction of 1,2-dihydroxyarenes with the corresponding α,ω-dihalo derivatives in refluxing 1-butanol in the presence of alkali hydroxides. The yields reach up to 62%.



1



2

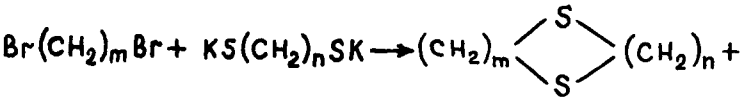


6a

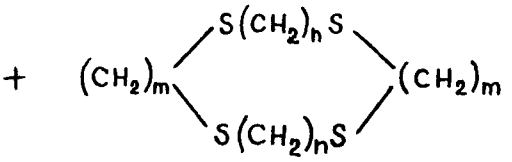
Instead of α,ω-dihaloalkanes, the corresponding ditosyl derivatives may be used from which heterocyclic polyethers *2* are obtained in 45% yield.[44–47] The high yields of crown ethers are explained by a "template" ("matrix") effect caused by coordination of the alkali metal ion with oxygen atoms during the polyether cyclization. Under similar conditions, oligothiamacrocycles are formed from α,ω-dithiols in only negligible yield (less than 2%).[48] This is due to the absence of the "template" effect owing to

the weak affinity of sulfur to alkali ions.[49] Thus, the 18-membered 1,4,7,10,13,16-hexathiacyclooctadecane *6a* was prepared by reaction of 1,2-ethanedithiol with 1,2-dibromoethane in 1.4% yield.[50,51]

The reaction of α,ω-dihaloalkanes with alkali α,ω-alkanedithiolates affords dithiacycloalkanes, their dimers (tetrathiamacrocyclanes) *4b–4g*, or linear polymers.[50] The condensation product ratio depends on the chain length of the starting reactants and the reaction conditions.



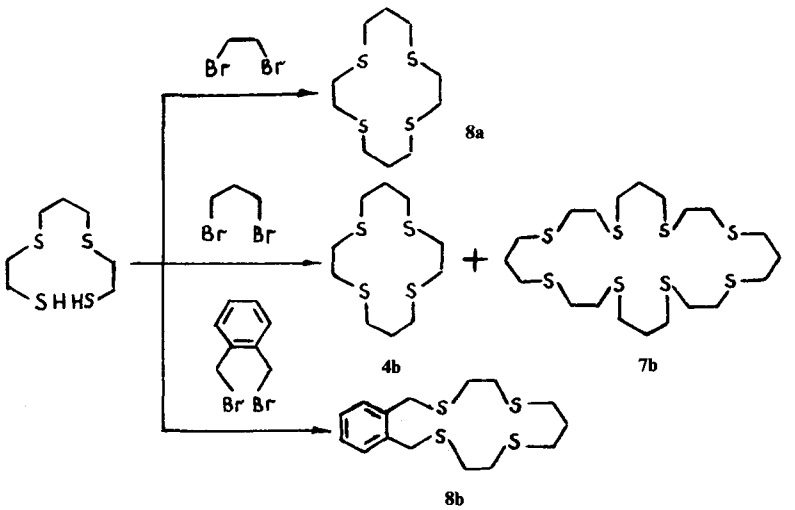
m = 2, n = 1–3
m = 3, n = 1–4



4b–4g

m = 2, n = 3–5
m = 3, n = 3, 4, 6

1,2-Ethanedithiol and 1,3-propanedithiol react with dichloromethane, 1,2-dibromoethane, and 1,3-dibromopropane to form mainly 5-, 6-, and 7-membered heterocycles. The reaction of 1,2-ethanedithiol or 1,3-propanedithiol with 1,4-dibromobutane, 1,5-dibromopentane, or 1,6-dibromohexane gives the dimeric compounds (tetrathiamacrocyclanes) *4b–4g* (Table 1). In this case, however, the yields of



8a

4b

7b

8b

TABLE 1

Monomacroheterocyclic sulfides

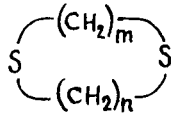
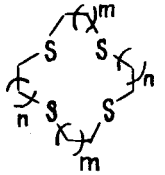
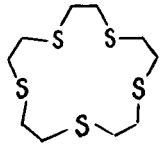
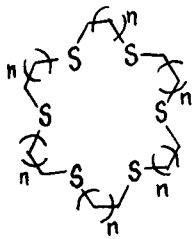
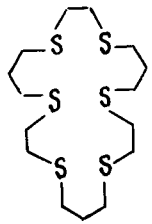
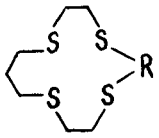
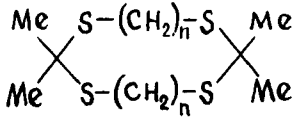
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
	m = n = 5		*3a*			49
	m = n = 6		*3b*		56	49,52
	m = 6, n = 8		*3c*		41	52
	m = 6, n = 10		*3d*		53	52
	m = n = 10		*3e*			49,58
	m = n = 1		*4a*			48,49
	m = 1, n = 2		*4b*			
	m = n = 2		*4c*	46	1.0	48,49,53
	m = 3, n = 1		*4d*			48
	m = 4, n = 1		*4e*			48
	m = 3, n = 2		*4f*	61	1.8	48,53
	m = 5, n = 2		*4g*	62	1.1	48,53
	m = 3, n = 3		*4h*	31–32	3.9	49
	m = 4, n = 4		*4i*	33–33.5	5.3	49
	m = 5, n = 5		*4j*	30–32	3.9	49
			*5*	97.5–99	11.0	49,58

TABLE 1 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
	1		*6a*	91–93	35	49,50,53
	2		*6b*	29–30	15.1	49
	3		*6c*	67–70	1.7	49
	4		*6d*	36.5–38	6.8	49
	5		*6e*	56–59.5	3.2	49
	1		*7a*	64–65	97	49
	2		*7b*			54–56,65
		CH_2CH_2	*8a*			54–56
			*8b*			54–56
						
	5		*9a*		52	70–72
	7		*9b*			68,69
	9		*9c*			68,69
	10		*9d*			68,69

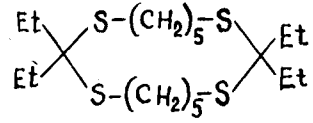
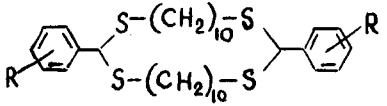
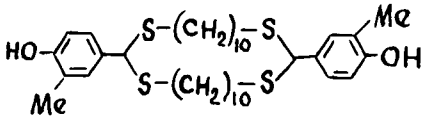
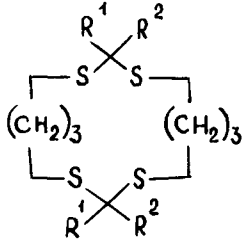
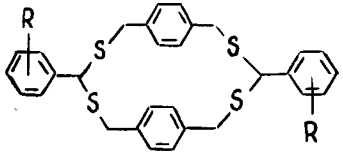
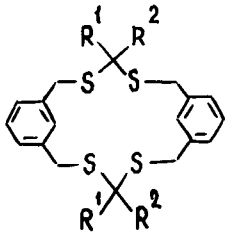
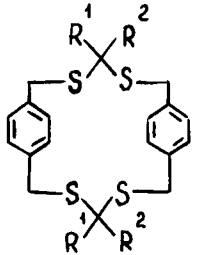
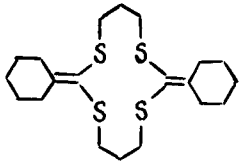
		*10*		52	70–72
	H	*11a*			68,69
	p-Cl	*11b*			68,69
	m-NO_2	*11c*			68,69
		*12*			68,69
	R^1 = H, R^2 = Ph	*13a*			73
	R^1 = R^2 = Me	*13b*	119–120	52	73
	R^1 = Me, R^2 = Et	*13c*			73
	R^1 = Me, R^2 = Ph	*13d*			73
	R^1 = R^2 = Et	*13e*			73
	H	*14a*	248–249		70–72
	p-Me	*14b*	266		70–72
	m-Me	*14c*	219–220		70–72
	p-OH	*14d*	262–264		70–72
	m-OH	*14e*	251–252		70–72
	m-C_6H_4COO	*14f*	169		70–72
	p-C_6H_4COO	*14g*	233		70–72

TABLE 1 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
		$R^1 = R^2 = H$	*15a*			73
		$R^1 = H$, $R^2 = Me$	*15b*			73
		$R^1 = H$, $R^2 = Ph$	*15c*	209–211	5	73
		$R^1 = H$, $R^2 = o\text{-}C_6H_4Me$	*15d*			73
		$R^1 = R^2 = Me$	*15e*	249–250	35	73
		$R^1 = Me$, $R^2 = Et$	*15f*	177–180	28	73
		$R^1 = Me$, $R^2 = Ph$	*15g*	218–220	25	73
		$R^1 = R^2 = Et$	*15h*	206–207	69	73
		$R^1 = H$, $R^2 = Ph$	*16a*	239–240	65	73
		$R^1 = R^2 = Me$	*16b*			73
			*17*	129.5	28.5	74

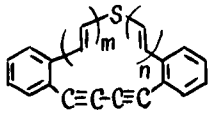
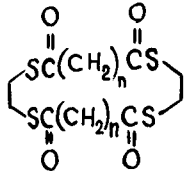
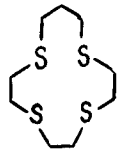
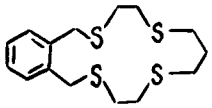
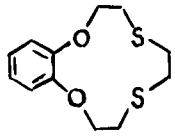
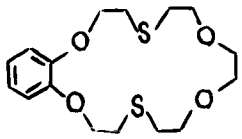
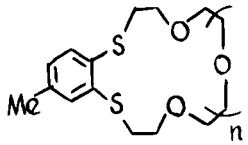
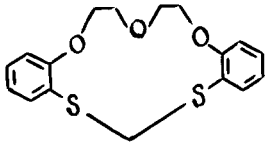
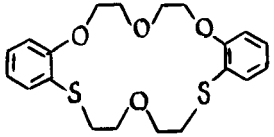
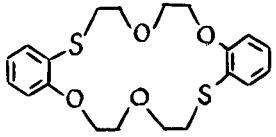
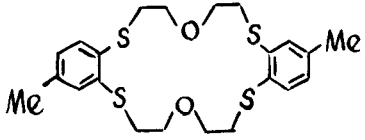
	m = n = 1 m = 1, n = 2 m = n = 2	*18a* *18b* *18c*	164 (dec.) 141 (dec.) 196 (dec.)	*17* 21 20	76,77 76,77 76,77
	3 5 7 8	*19a* *19b* *19c* *19d*	118–120	38 9 14 18	75 75 75 75
		*20*			54–56
		*21*			54–56
		*22*	92	34	79
		*23*	91	1	78,79

TABLE 1 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
	1 2		*24* *25*	oil oil	30 56	78 78,79
			*26*	150–153	3	78,79
			*27*	143–144	15	78,79
			*28*	114–115	5	78,79
			*29*	147	6	78,79

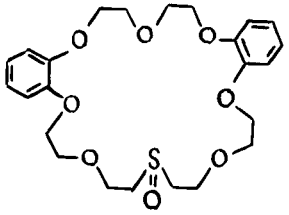
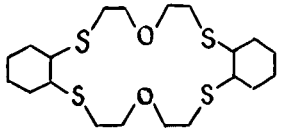
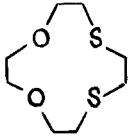
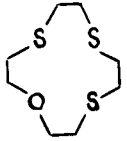
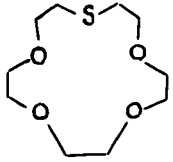
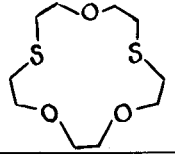
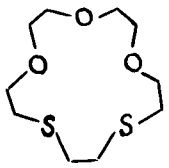
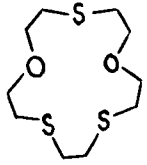
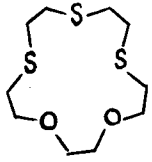
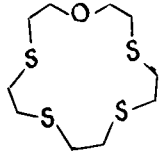
	*30*	133	33	78
	*31*	oil	30	78,79
	*32*	20–24	19	82
	*33*	89–90	26	82
	*34*	oil	29	82
	*35*	oil	27	82

TABLE 1 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
			*36*	51–52	20	82
			*37*	oil	5	81
			*38*	43–44	41	81
			*39*	93–95	13	81

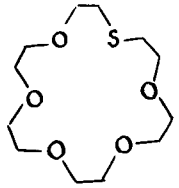
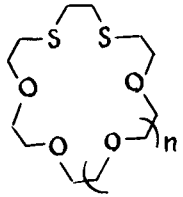
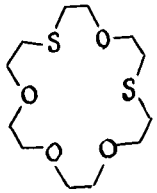
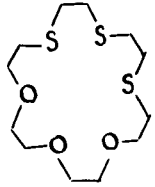
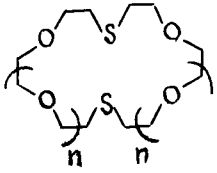
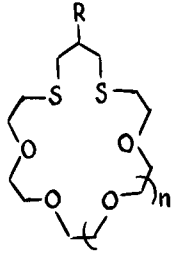
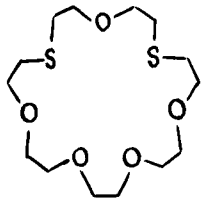
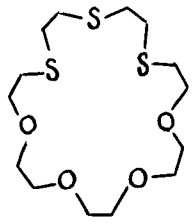
		*40*	oil	36	81
	1 2	*41a* *41b*	54–56 oil	28 5	81 80
		*42*	oil	29	81
		*43*	oil	11	81
	1 2	*44a* *44b*	90–91 oil	12 1	82,84 80

TABLE 1 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
	1	H	*45a*	oil	24	80
	1	OH	*45b*	oil	8	80
	2	OH	*45c*	oil	15	80
			*46*	oil	25	81
			*47*	oil	11	81

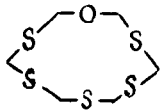
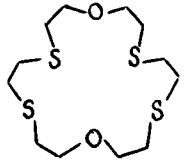
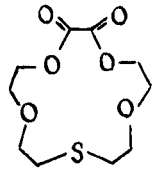
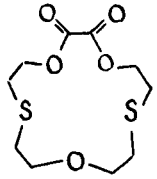
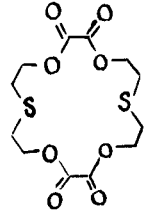
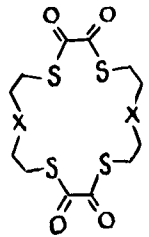
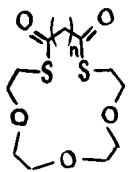
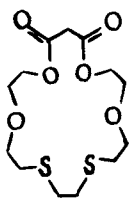
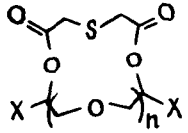
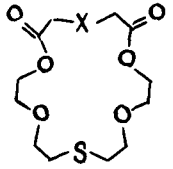
	*48*	163–165		85
	*49*	89–90	1.7	50
	*50*	88–90	5.7	88
	*51*	45	7.7	88
	*52*	195–203	14	88

TABLE 1 (*Continued*)

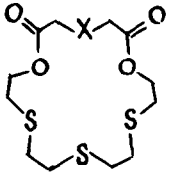
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
		O	*53a*	207–210	67	88
		S	*53b*	108–109	62	88
	1		*54a*			85
	2		*54b*	oil		85
	1		*55a*	oil	85	85
	2		*55b*	oil	80	85



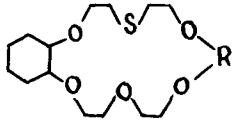
1	H	*56a*	93.5–94.5	4.8	86
2	H	*56b*	85.5–86.5	23	86
3	H	*56c*	43.5–44.5	20	86
4	H	*56d*	204 (0.2)	23.1	86
1	Et	*56e*	96.5–97.5	6	89
2	Et	*56f*	121.5–122.5	20	89
3	Et	*56g*	[184–195 (1.3)]	34	89
4	Et	*56h*	[180–181 (1.5)]	53	89



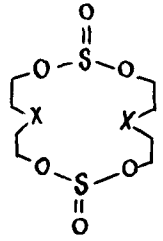
O	*57a*	113.5–115	35	86
S	*57b*	106–107	11	86



O	*58a*	36–36.5	20	86
S	*58b*	oil	31	86

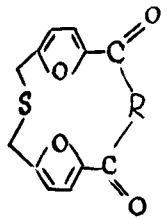
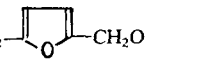


CH_2CH_2	*59a*	[165–170 (1.0)]	30	89
	*59b*	[220 (1.0)]	28	89



O	*60a*			94
S	*60b*			94

TABLE 1 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
		$O(CH_2)_2O$	*61a*	157–158	16	95
		$[O(CH_2)_2]_3O$	*61b*	212–214	54	95
		$[O(CH_2)_2]_4O$	*61c*	190–191	13	95
		$[O(CH_2)_2]_5O$	*61d*	215–217	28	95
		$[O(CH_2)_2]_6O$	*61e*	218–219	36	95
		$[O(CH_2)_2]_2S$	*61f*	200–201	57	95
		o-OC_6H_4O	*61g*	46–48	77	95
		m-OC_6H_4O	*61h*	69–70	30	95
		p-OC_6H_4O	*61i*	66–68	11	95
		$S(CH_2)_2S$	*61j*	218–220	29	95
		cis-$OCH_2CH{=}CHCH_2O$	*61k*	192–193	70	95
		trans-$OCH_2CH{=}CHCH_2O$	*61l*	185–186	30	95
		$OCH_2C{\equiv}CCH_2O$	*61m*	216–218	60	95
		$O(CH_2)_6O$	*61n*	212–213	45	95
		$OCH_2CH(Me)O$	*61o*	185–186	53	95
		$OCH(Me)CH(Me)O$	*61p*	205–206	50	95
		$OCH(Me)CH_2CH_2O$	*61q*	214–215	65	95
		$OCH_2C(Me)_2CH_2O$	*61r*	216–217	52	95
		$OCH_2CH(Me)OCH(Me)CH_2O$	*61s*	218–220	37	95
			*61t*	310–312	57	96
		$OCH_2CH_2OCH_2C{\equiv}CCH_2OCH_2CH_2O$	*61u*	218–220	43	96
		$O(CH_2CH_2O)_2CH_2C$ $\|\|\|$ $O(CH_2CH_2O)_2CH_2C$	*61v*	220–221	36	96
		$O(CH_2CH_2O)_3CH_2C$ $\|\|\|$ $O(CH_2CH_2O)_3CH_2C$	*61w*	217–218	12	96
		trans-$OCH_2CH_2OCH_2CH$ $\|\|$ $OCH_2CH_2OCH_2CH$	*61x*	223–224	40	96
		trans-$O(CH_2CH_2O)_2CH_2CH$ $\|\|$ $O(CH_2CH_2O)_2CH_2CH$	*61y*	210–211	32	96

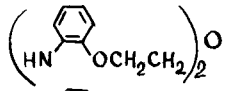
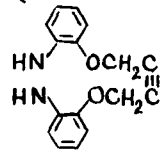
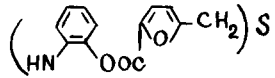
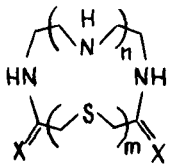
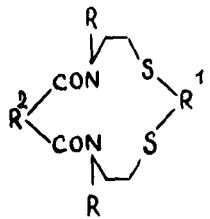
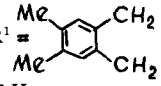
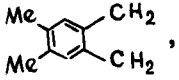
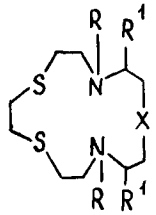
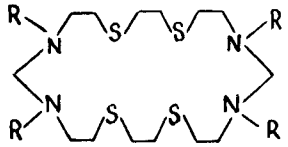
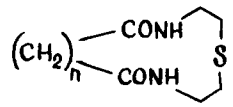
		$NH(CH_2)_2NH$	*62a*	210–212	50	97
		$NH(CH_2)_3NH$	*62b*	72–73	22	97
		$NH(CH_2)_6NH$	*62c*	87–88	50	97
		o-NHC_6H_4NH	*62d*	197–198	97	97
		m-NHC_6H_4NH	*62e*	204–205	80	97
		p-NHC_6H_4NH	*62f*	224–225	91	97
		$NH(CH_2)_2S(CH_2)_2NH$	*62g*	45–46	93	97
		NC_6H_5	*62h*	184–185	97	97
		N-aminophthalimide	*62i*	88–89	62	97
			*62j*	230–231	53	96
			*62k*	218–219	69	96
			*62l*	225–227	83	96
	m = 1, n = 2	O	*63a*	174.5–176.5	15.4	98
	m = 1, n = 2	H_2	*63b*	oil	60	98
	m = 2, n = 1	O	*63c*	194–196	40.9	98
	m = 2, n = 1	H_2	*63d*	62.5–65	80	98
	m = 2, n = 2	O	*63e*	148.5–151	28.5	98
	m = 2, n = 2	H_2	*63f*	oil	80	98
		R = H, $R^1 = CH_2CH_2$, $R^2 = (CH_2)_4$	*64a*	170 –171	65	103
		R = $PhCH_2CH_2$, $R^1 = CH_2CH_2$, $R^2 = (CH_2)_4$	*64b*	134–135	70	103
		R = $MeOOCCH_2CH_2$, $R^1 = CH_2CH_2$, $R^2 = (CH_2)_4$	*64c*	105–107	68	103
		R = $NCCH_2CH_2$, $R^1 = CH_2CH_2$, $R^2 = (CH_2)_4$	*64d*	184–185	70	103
		R = H, $R^1 = CH_2CH_2$, $R^2 = o$-C_6H_4	*64e*	181–182	66	99–101

TABLE 1 (*Continued*)

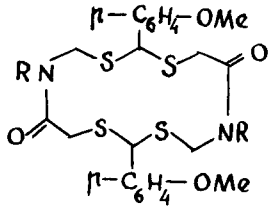
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
		R = $PhCH_2CH_2$, R^1 = CH_2CH_2, R^2 = *o*-C_6H_4	*64f*	190–191	70	103
		R = $MeOOCCH_2CH_2$, R^1 = CH_2CH_2, R^2 = *o*-C_6H_4	*64g*	oil	70	99–101
		R = $NCCH_2CH_2$, R^1 = CH_2CH_2, R^2 = *o*-C_6H_4	*64h*	oil	70	103
		R = H, R^1 =  R^2 = *o*-C_6H_4	*64i*	135–136	50	102
		R = $MeOOCCH_2CH_2$, R^1 =  , R^2 = *o*-C_6H_4	*64j*	72–73	55	102,103
		R = $MeOOCCH_2CH_2$, R^1 = CH_2CH_2, R^2 = $(CH_2CH_2S)_2CH_2CH_2$	*64k*	oil	60	104
		R = H, R^1 = CH_2CH_2S—SCH_2CH_2 R^2 = bond	*64l*	135	80	99–101
		R = $MeOOCCH_2CH_2$, R^1 = CH_2CH_2S—SCH_2CH_2, R^2 = bond	*64m*	oil	60	103
		R = H, R^1 = Ph, X = CO	*65a*	oil	60	113
		R = R^1 = H, X = SO_2	*65b*		65	113
		R = CH_2CH_2COOMe, R^1 = Ph X = CO	*65c*			



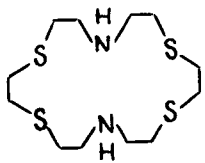
	$PhCH_2CH_2$	*66a*	oil	63	114
	$MeOOCCH_2CH_2$	*66b*	oil	60	114
	$NCCH_2CH_2$	*66c*	oil	65	114



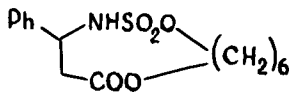
7		*67a*	156–157	42	105
8		*67b*	131–132	35	105



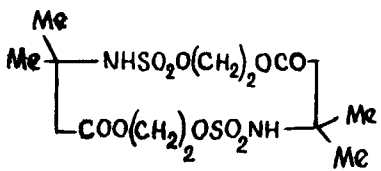
	H	*68a*	214–217	61	106
	Me	*68b*	206–208	97	106



		69	125	45	53,107

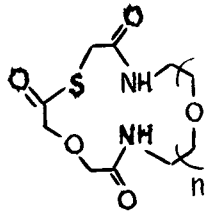
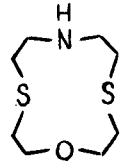
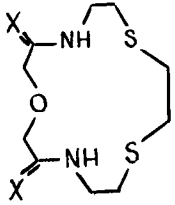


		70	125–127	8.7	108,109



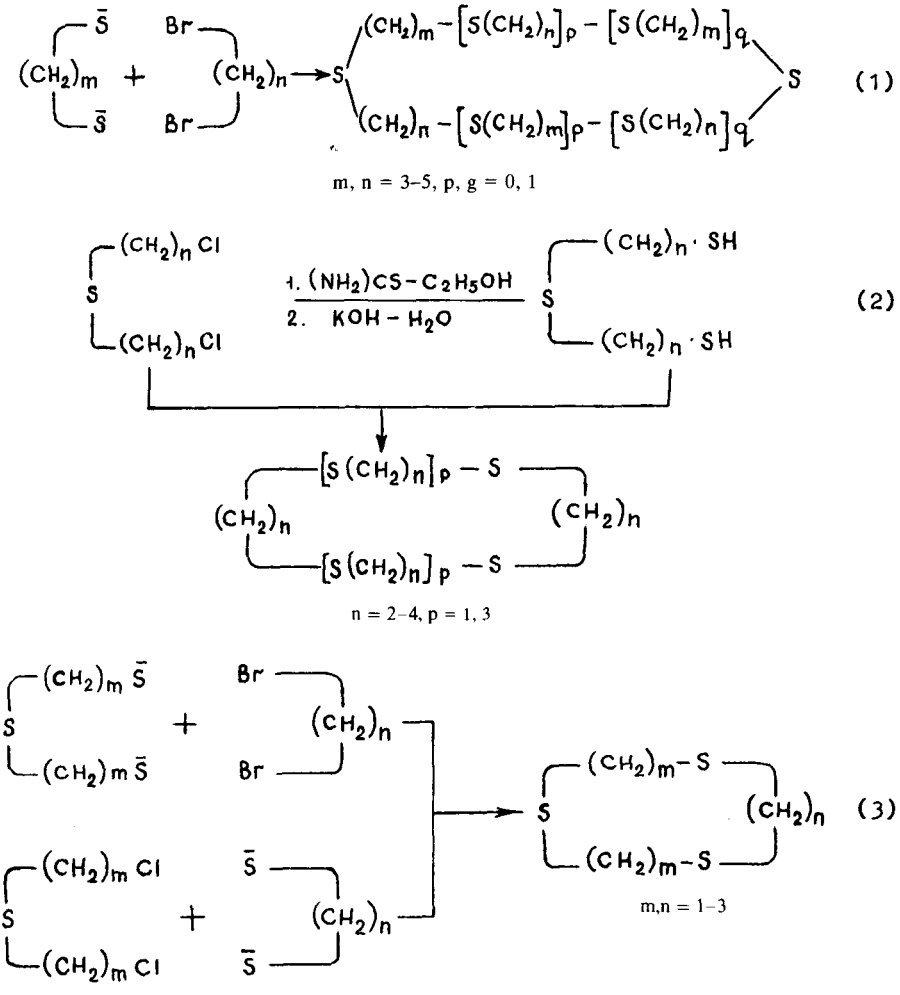
		71	203–204		108,109

TABLE 1 (*Continued*)

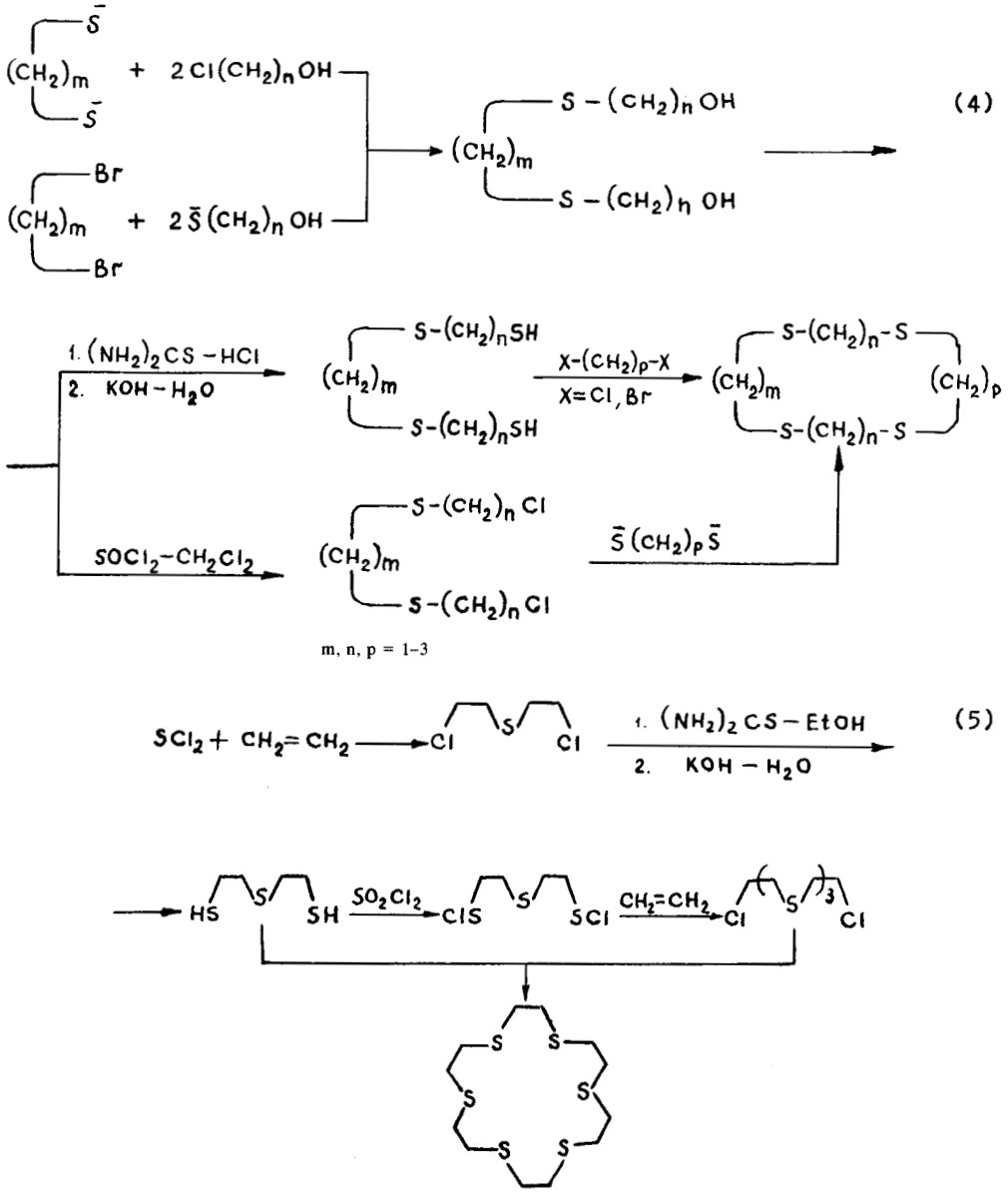
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Ref.
1	2	3	4	5	6	7
	1		*72a*	140–141	35	110
	2		*72b*	132–133	30	110
			*73*	64	18	111
		O	*74a*	158	45	112
		H_2	*74b*	oil		112

tetrathiamacrocycloalkanes do not exceed 1.8%. The formation of medium sized rings is not observed in the above reactions. A high dilution of the reaction mixture has allowed the method for preparing oligothiamacrocycloalkanes to be modified.[52] Thus, in the reaction of 1,6-dibromohexane or 1,10-dibromodecane with 1,6-hexanedithiol, 1,8-octanedithiol, or 1,10-decanedithiol with large excess of solvent the yields of the corresponding dithiamacrocycles *3b–3e* reach 41–69% (Table 1). Under analogous conditions, thia-18-crown-6 (*6a*) was obtained in 31% yield.[53] The oligothiamacrocycloalkanes *7b*, *8a*, and *8b* have been prepared by reaction of 3,7-dithia-1,9-nonanedithiol with the corresponding α,ω-dibromoalkanes.[54–56]

General synthetic routes to oligothiamacrocycloalkanes suggested by Okhrimovych *et al.*[49,58] are presented in Scheme 1.



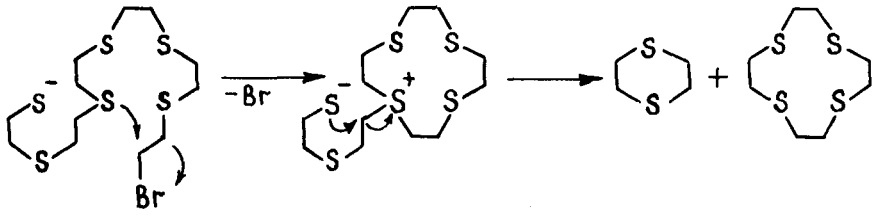
SCHEME 1



SCHEME 1 (*continued*)

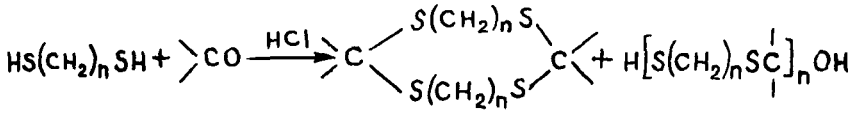
Method (1) is most suitable for the synthesis of tetrathia- and hexathiacycloalkanes with the sulfur atoms separated by tetra- and pentamethylene bridges. At the same time, methods (3) and (5) lead to the highest yields of oligothiamacrocycloalkanes consisting of alternating SCH_2CH_2 groups. Along with 1,4,7,10,13,16-

hexathiacyclooctadecane (*6a*) reactions (1) and (3) give, quite unexpectedly, 1,4-dithiane and 1,4,7,10-tetrathiacyclododecane *4a*. This is explained by the formation of a cyclic sulfonium ion due to intramolecular cyclization.[49]



Use of the methods (2), (4), and (5) minimizes the amount of by-products. The compounds *3a*, *3b*, *4a–4c*, and *4h–7a*, synthesized by these methods, are shown in Table 1. The effect of the ring size and structure in these compounds as well as the solvent effect on the complexation with Cu^{2+} have been discussed.[59–63] The possible application of oligothiamacrocycloalkanes as extractants of silver and mercury salts has been studied.[64–67]

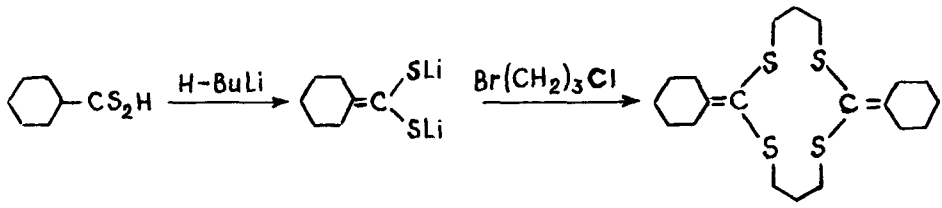
In the presence of acid catalysts α,ω-alkanedithiols react rapidly, but irreproducibly, with carbonyl compounds to form either macroheterocyclic dimercaptals and dimercaptols or linear polymers.



In this way, 20-, 24-, and 26-membered macroheterocycles have been prepared from 1,7-hexane-, 1,9-nonane-, and 1,10-decanedithiol. Acetone, benzaldehyde, *m*-nitrobenzaldehyde, and vanillin have been used as carboxylic compounds. The yields of the macroheterocycles *9b–9d*, *11a–12* were 48–98.9%. No polymeric products are formed in this case. However, the use of benzaldehyde diethyl acetal and *p*-chlorobenzaldehyde diethyl acetal instead of the corresponding aldehydes leads to polymers in 69.5 and 60% yield, respectively.[68,69]

The 16-membered sulfur-containing heterocycles *9a* and *10* have been obtained in 52% yield by reaction of 1,5-pentanedithiol with acetone or diethyl ketone. The reaction of 1,4-bis-(mercaptomethyl)benzene with aromatic aldehydes leads to the macrocyclic aromatic mercaptals *14a–14g*. For the synthesis of the latter a mixture of dithiol and a carbonyl compound was treated with gaseous hydrogen chloride in the absence of solvent. In this case the yields of the end products were irreproducible. Later on this reaction was carried out in ether solution.[73] The reaction proceeds more efficiently in the presence of boron trifluoride etherate or methanolic sulfuric acid as catalyst.

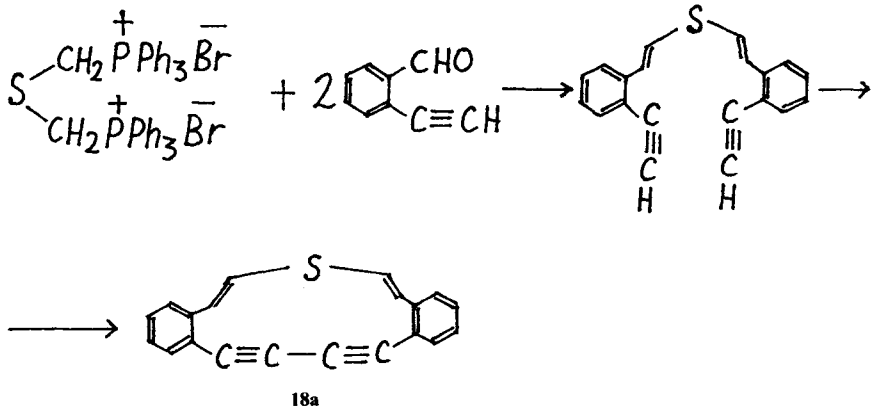
2,8-Bis(cyclohexylidene)-1,3,7,9-tetrathiacyclododecane *17* has been prepared from cyclohexanedithiocarboxylic acid.[74]



17

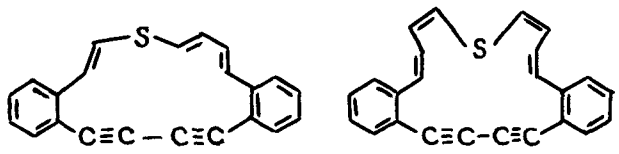
The yields and melting points of the oligothiamacrocycloalkanes *9a–17* are presented in Table 1.

A number of sulfur-containing annulenes *18a–18c* have been prepared by oxidative coupling of bis-2-[(2-ethynylphenyl)-vinyl] sulfide and its vinyl analogs.[76,77] Thus, the reaction of bis-[(triphenylphosphonia)methyl] sulfide dibromide with *o*-ethynylbenzaldehyde gives the corresponding diethynyl derivative, the oxidation of which in the presence of copper acetate in pyridine leads to the macroheterocycle *18a*.



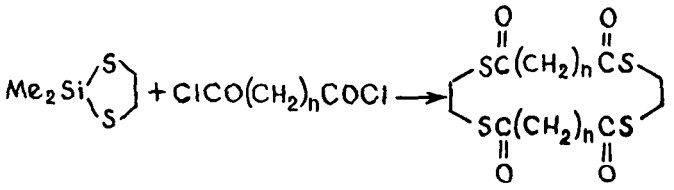
18a

Compounds *18b* and *18c* have been obtained in a similar manner (Table 1).



18b 18c

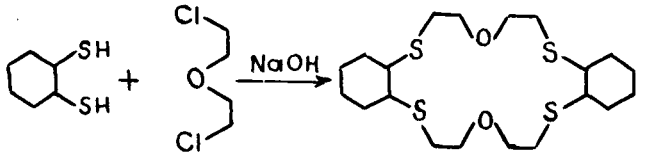
The synthesis of the macroheterocyclic thiolactones *19a–19d* was performed using the reaction of 2,2-dimethyl-2-sila-1,3-dithiacyclopentane with α,ω-alkanedicarboxylic acids dichlorides[75] (Table 1).



n = 3, 5, 7, 8 **19a–19b**

1.2. Oxathiamacrocycloalkanes

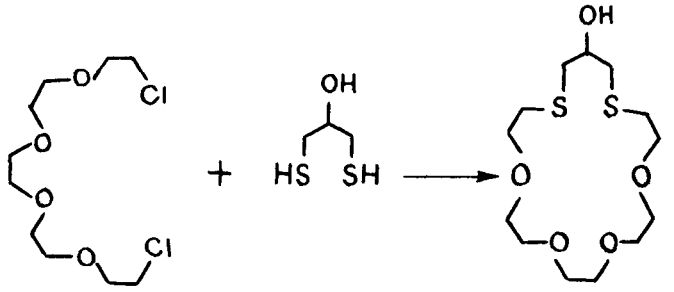
Crown ethers containing ring sulfur atoms along with oxygen atoms were first described by Pedersen.[78,79] This author also showed that the substitution of oxygen atoms by sulfur atoms weakens the complexing ability of crown ethers towards potassium and sodium ions and increases that toward silver ions. Thiacrown ethers were prepared by cyclization of aromatic 1,2-dithiols or *o*-mercaptophenol with aliphatic α,ω-dihalo derivatives. For the synthesis of the above compounds the reaction of *o*-dihaloarenes with α,ω-alkanedithiols was also used. *trans*-1,2-Cyclohexanedithiol reacts with β,β'-dichlorodiethyl ether analogously to aromatic 1,2-dithiols to form 2,8,15,21-tetrathia-5,18-dioxatricyclo[20.4.0.0^{9,14}]hexacosane *31*.



31

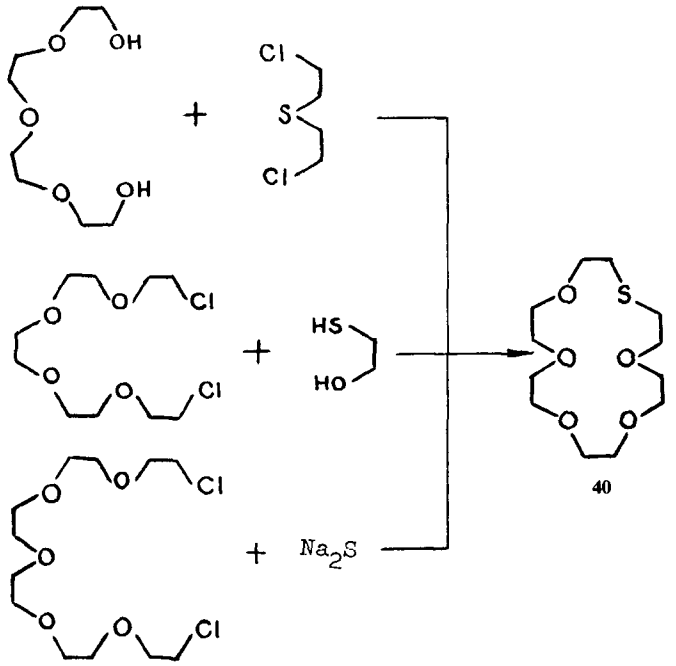
The yields and melting points of the thiacrown ethers *22–31* synthesized are given in Table 1.

For the synthesis of thiacrown ethers the reaction of α,ω-alkanedithiols with α,ω-dichlorooligoethylene glycols was used. For example, the macroheterocycle *45b* was obtained in 8% yield by cyclization of 1,14-dichloro-3,6,9,12-tetraoxatetradecane with 1,3-dimercapto-2-propanol.[80]

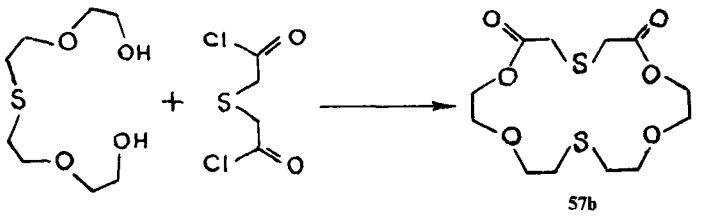


45b

The reactions of sodium sulfide and 2-mercaptoethanol with bis(2-chloroethyl) ether and bis(2-chloroethyl) ethers of oligoethylene glycols as well as that of bis(2-chloroethyl) sulfide with oligoethylene glycols are of synthetic interest[81–84] (compounds *32–49*, Table 1).



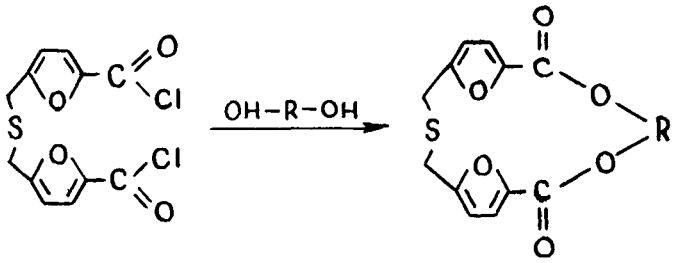
The reaction of oligoethylene thioglycols or α,ω-alkanedithiols with aliphatic α,ω-dicarboxylic acid dichlorides (oxalic, malonic, succinic, and 3-thiaglutaric) gave under high dilution over twenty thiacrown ethers containing ester groups in the ring.[85–89]



Earlier the interest in macrocyclic lactones was caused first of all by the possibility of their application as fragrant substances in perfumery.[35] Nowadays, due to the discovery of a natural macrocyclic antibiotic, valinomycin, containing CO groups in the ring and displaying a unique complexing ability towards alkali ions,[21] these compounds have attracted much attention as complexing agents. They possess a very

high complexing ability for ions of alkali and alkali earth metals. Isostructural sulfur-containing macroheterocycles also form complexes with Na^+, K^+, Ag^+, Rb^+, Cs^+, and Ba^{2+} [90–93] (compounds *50–59b*, Table 1).

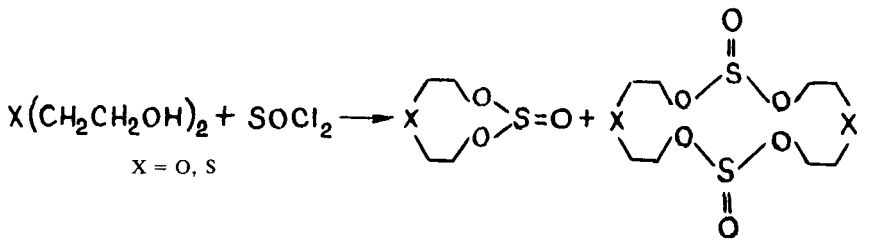
A series of sulfur-containing macroheterocycles have been synthesized from difurfuryl sulfide 5,5′-dicarboxylic dichloride as the key compound.[95–97] Various diols (pyrocatechol, resorcinol, hydroquinone, mono- and triethylene glycol, 2,2-dimethyl-3-oxa-1,5-pentanediol, *cis*- and *trans*-2-butene-1,4-diol, and 2-butyne-1,4-diol) as well as 1,2-ethanedithiol were used as the second reagent (compounds *61a—61y*, Table 1).



61a–61y

The reaction is carried out in refluxing *N,N*-dimethylformamide in the presence of lithium hydride. The yields of macroheterocycles amount to 11–77%.

The cyclization of diethylene glycol or thiodiglycol with thionyl chloride leads to the medium- and macroheterocycles *60a* and *60b*.[94]

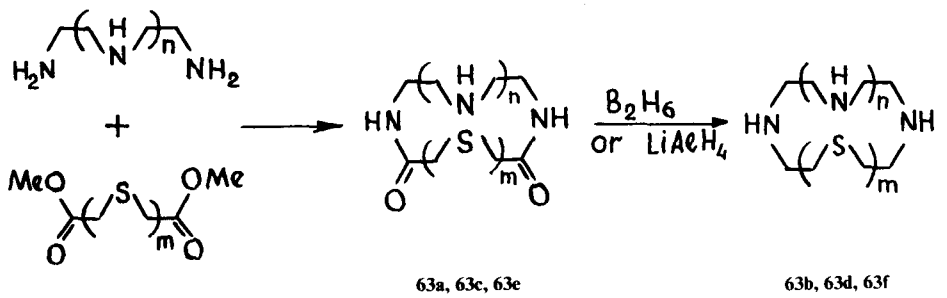


60a, 60b

1.3. Thiaazamacrocycloalkanes

A general method for the synthesis of thiaazamacrocycloalkanes in 60–80% yield is based on the reaction of available thia-α,ω-alkanedicarboxylic acid dimethyl esters with polyethylene polyamines, followed by reduction of the macroheterocyclic diamides obtained with $LiAlH_4$ or B_2H_6 in tetrahydrofuran.[98]

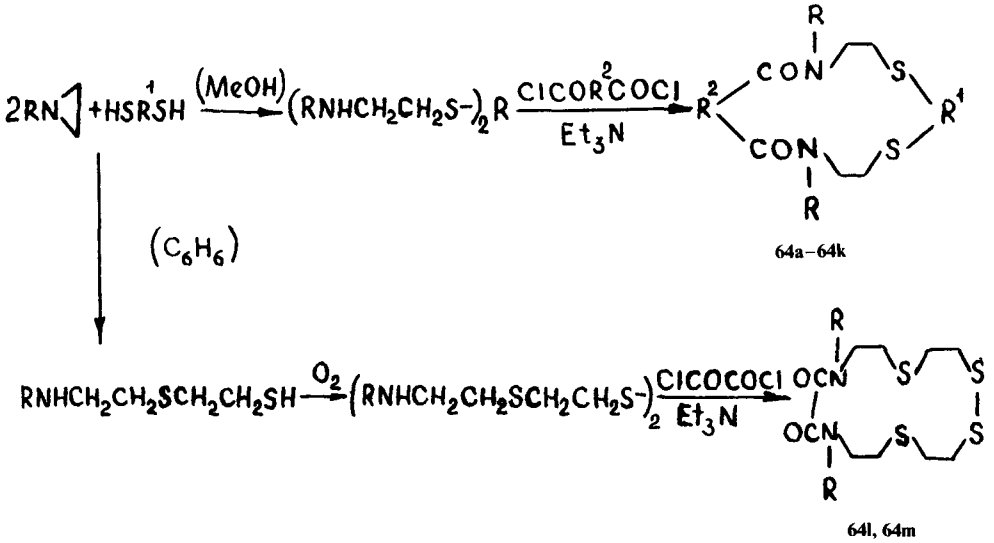
In this way, several sulfur-containing macroheterocyclic diamides (*63a*, *63c*, *63e*) have been prepared in 15.4–40.9% yield. In this case the reaction is carried out during 3–7 days without high dilution of the reaction mixture. The cyclization proceeds only



63a, 63c, 63e 63b, 63d, 63f

at the terminal primary amino groups without affecting less reactive secondary amino groups.

The present authors[99–104] have found a new synthetic route to sulfur-containing alkyl and functionally substituted open-chain and macroheterocyclic diamines. *N*-Substituted open-chain diamines are available from the reaction of *N*-substituted aziridines with 1,2- or 1,4-dithiols in an appropriate solvent. In methanol at 60 °C this reaction leads to the corresponding sulfur-containing open-chain diamines. Use of an aprotic solvent (benzene), however, results in monoadducts which can be readily oxidized to the corresponding disulfides (Scheme 2).



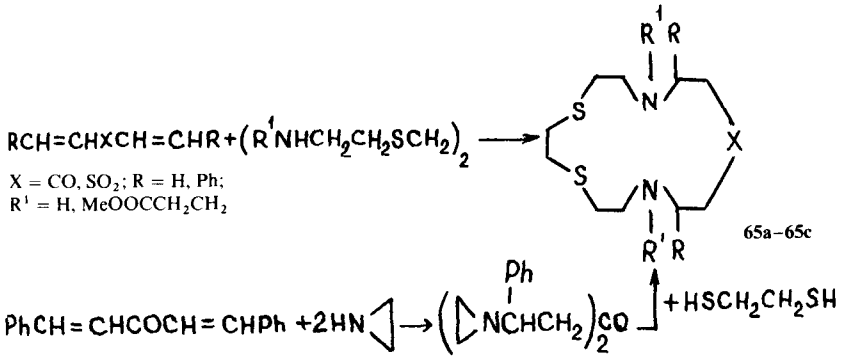
64a–64k

64l, 64m

SCHEME 2

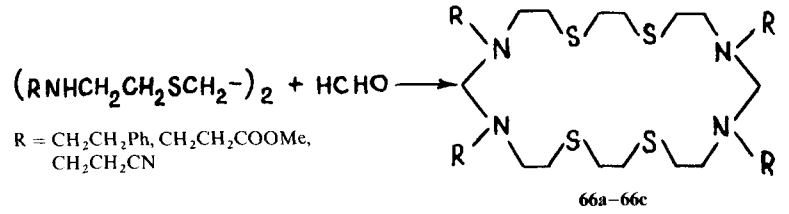
In order to obtain macroheterocyclic compounds containing aralkyl and functional groups at the nitrogen atoms, the cyclization of the diamines prepared from dicarboxylic acid dichlorides has been studied. The reaction is carried out in dry benzene in high dilution. *N*-Unsubstituted macroheterocycles as well as macroheterocyclic compounds containing phenethyl, carbomethoxyethyl, or cyanoethyl groups at the nitrogen atoms (*64a–64m*) are given in Table 1.

The 15-membered thiaazamacrocyclanes *65a* and *65b* were prepared by cyclization of open-chain diamines with dibenzalacetone and divinyl sulfone at 60 °C in methanol with high dilution.

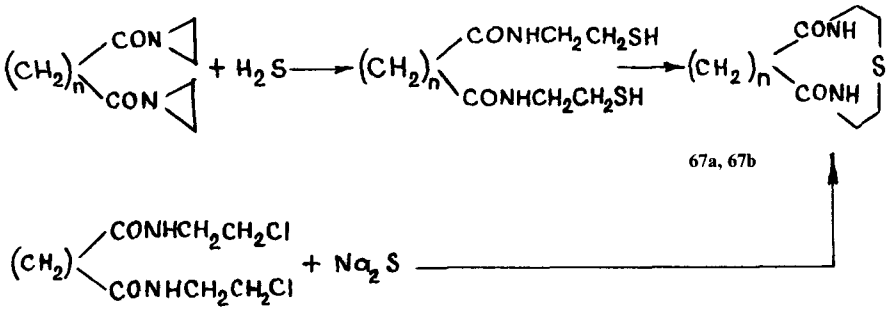


Compound *65a* was also prepared by reaction of bis(2-phenyl-2-aziridinoethyl) ketone with 1,2-ethanedithiol. The cyclization occurs at 60 °C under high dilution. Both reactions afford polymeric products in yields from 5 to 20%.%.

The 22-membered aminals *66a–66c* have been synthesized in 60–65% yield by reaction of linear diamines with formaldehyde in boiling methanol with high dilution.

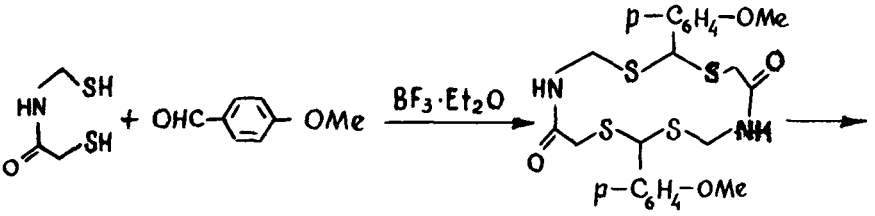


The reaction of the bis-*N*-ethylene amides of azelaic and sebacic acid with excess hydrogen sulfide affords the macrocyclic sulfides *67a* and 67b, along with the bis(β-mercaptoethyl)diamides of the corresponding acids.[105]

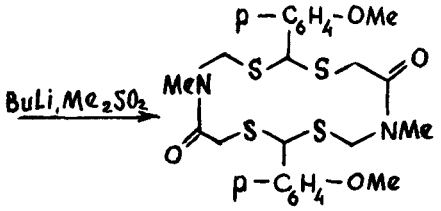


These macrocyclic compounds seem to be the products of an intramolecular opening of the aziridine rings by a mercapto group in the intermediate *N,N*-ethylene-*N'*-(β-mercaptoethyl)diamides of azelaic and sebacic acid. The cyclic sulfide *67a* has been further synthesized by reaction of the bis(β-chloroethyl)diamide of azelaic acid with sodium sulfide.

The cyclization of the *N*-(mercaptomethyl)amide of thioglycolic acid with anisaldehyde leads to the macrocycle *68a*.[106]

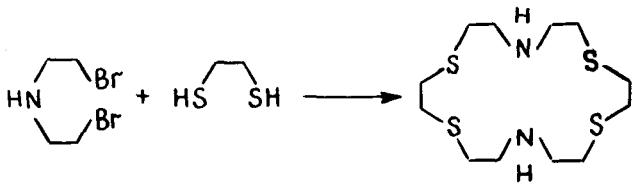


68a



68b

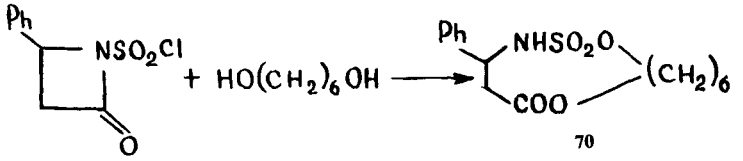
The thiaazamacrocycloalkane *69* has been synthesized in 45% yield by reaction of bis(2-bromoethyl)amine with 1,2-ethanedithiol.[53,107]



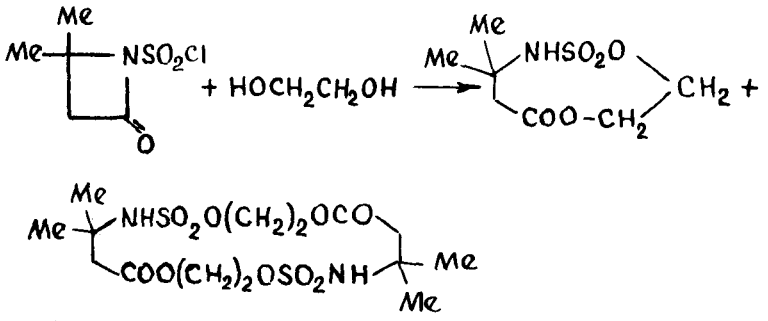
69

1.4 Oxathiaazamacrocycloalkanes

The reaction of *N*-chlorosulfonyl-β-lactams with glycols leads to the formation of the new macroheterocycles *70* and *71*.[108,109]

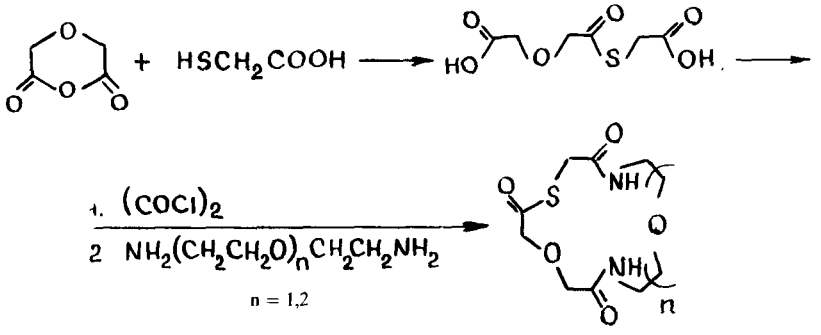


70



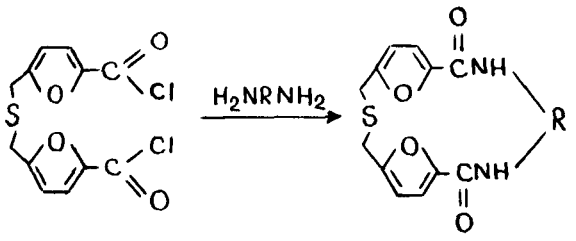
71

Macroheterocycles containing O, N, and S atoms in the molecule have been synthesized from 5-oxo-3-oxa-6-thiahexanedicarboxylic acid which is the product of the reaction of diglycolic acid anhydride with thioglycolic acid.[110] The dicarboxylic acid thus obtained, when treated with oxalyl chloride, forms the corresponding dichloride. The reaction of the latter with 3-oxa-1,5-diaminopentane or 3,6-dioxa-1,8-diaminooctane in high dilution gives the macroheterocycles *72a* and *72b* in 30–35% yield.



72a, 72b

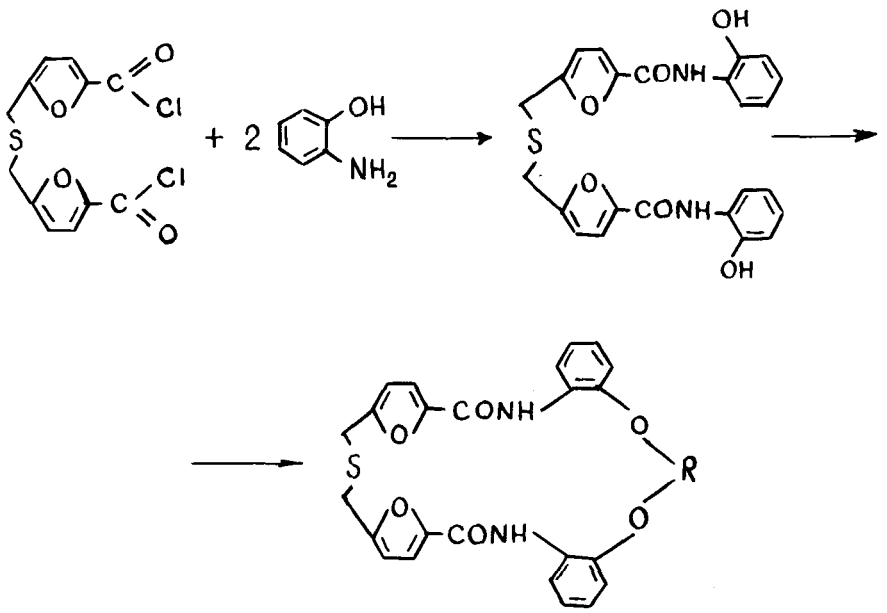
The corresponding macroheterocyclic diamides *62a–62i* have been prepared in an analogous way from the dichloride of difurfuryl sulfide 5,5′-dicarboxylic acid and aliphatic or aromatic diamines.[97]



62a–62g

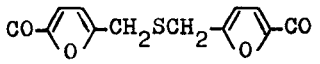
R = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_6$, $(CH_2)_2S(CH_2)_2$, *o*-C_6H_4, *m*-C_6H_4, *p*-C_6H_4

The synthesis of the oxathiaazamacrocyclanes *62j–62l* has also been reported.[96]



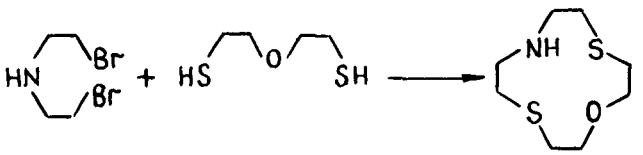
62j–62l

R = $CH_2CH_2OCH_2CH_2$, $CH_2C{\equiv}CCH_2$,



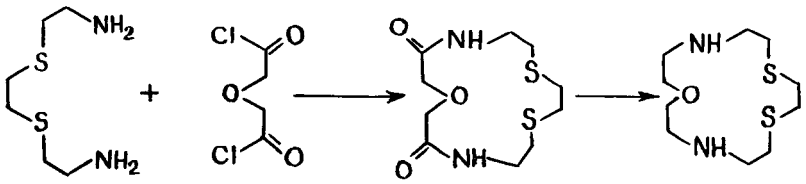
The reaction of difurfuryl sulfide 5, 5′-dicarboxylic dichloride with *o*-aminophenol leads to the corresponding diamide which, upon further cyclization with the dichloride (refluxing for 25–30 hours in the presence of potassium hydroxide) gives the macroheterocycles *62j–62l* in yields up to 83%.

The reaction of bis(2-bromoethyl)amine with 3-oxapentane-1,5-dithiol gives the oxathiaazamacrocyclane *73* in 18% yield.[111]



73

The oxathiaazamacrocycloalkane *74a* has been prepared by cyclization of 3,6-dithia-1,8-diaminooctane with 3-oxapentanedicarboxylic dichloride, followed by reduction of the cyclic diamide *74b* formed with diborane in tetrahydrofuran.[112]

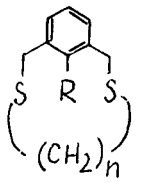


74b 74a

2. *Oligothiacyclophanes and Their Analogs*

2.1. *Oligothiacyclophanes*

Cyclophanes are cyclic compounds containing two or more polymethylene-bridged benzene rings. There are mononuclear cyclophanes in which the benzene ring is bound to the polymethylene system in the *o*-, *m*-, or *p*- position. The study of these compounds has given clues to the understanding of steric interactions of the benzene ring substituents, transannular effects in the ring, the dependence of the aromatic ring rotation barrier on the polymethylene bridge length, etc. The synthesis of a great number of mononuclear dithiacyclophanes *75a–79c* containing from 2 to 12 methylene groups and two sulfur atoms in the aliphatic bridge has been performed. The benzene rings of these compounds possess various intraannular substituents.[115–124] Analogous cyclophanes containing oxygen and sulfur atoms in the polymethylene bridge (*80a–80i*) have also been prepared.[119,122,123,125–127] The synthesis of dithiacyclophanes with n = 2 or 3 yields also the dimeric compounds *82a–82n* (Table 2).[116,119,122] According to the ^{1}H NMR data the steric requirements of the intracyclic group in the benzene ring are less strict than those in the methyl group. The bulk of CO_2Me and SO_2Me groups is somewhat larger than that of NO_2 and SMe groups, the latter being more bulky than the OMe group. Due to the steric factors the SOMe group is intermediate between the SO_2Me and SMe groups. The NH_2 group is similar in its bulk to the hydroxy group. The two substituents NO_2 and OH are more bulky than an aromatically bound fluorine atom and less bulky than the chlorine atom or the SMe and NO_2 group. The general steric requirements for the aromatically bound iodine atom are larger than for the chlorine or bromine atoms, but comparable with that for the SMe group.

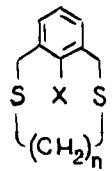


75a–79c

n = 2-12; R = Ph, I, NH_2, NO_2, OH, OMe, SMe, SOMe, SO_2Me

TABLE 2

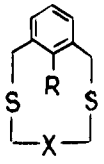
Oligothiacyclophanes and Their Analogs

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
	2	H	*75a*	85–86	7	116
	3	H	*75b*	100–101	40	116
	4	H	*75c*	83–84	21	117
	5	H	*75d*	59–60	36	116
	6	H	*75e*	63–64	32	116
	7	H	*75f*	51–52		118
	8	H	*75g*	28–30		118
	9	H	*75h*	25		118
	3	F	*75i*	71–72	16	116
	4	F	*75j*	59–60	16	117
	5	F	*75k*	96–97	41	116
	6	F	*75l*	81–82	29	116
	7	F	*75m*	49–50		118
	8	F	*75n*	20		118
	9	F	*75o*	58–59		118
	4	Cl	*75p*	76–77	9	117
	5	Cl	*75q*	99–100	35	116
	6	Cl	*75r*	111–112	37	116
	7	Cl	*75s*	83–84		118
	8	Cl	*75t*	53–54		118
	9	Cl	*75u*	38–40		118
	4	Br	*75v*	117–118	12	117
	5	Br	*75w*	86–87	47	116
	6	Br	*75x*	97–98	39	116
	7	Br	*75y*	75–76		118
	8	Br	*75z*	47–48		118
	9	Br	*76a*	28–30		118
	8	I	*76b*	44–47	17	119
	9	I	*76c*	20	9	119
	10	I	*76d*	20	11	119

6	OH	*76e*	113–114	4	119
7	OH	*76f*	108–110	5	119
2	MeO	*76g*		60	116
3	MeO	*76h*	134–135	66	120
4	MeO	*76i*	100–102	36	120
5	MeO	*76j*	99	74	120
6	MeO	*76k*	106	65	120
7	MeO	*76l*	45–47	58	120
8	MeO	*76m*	35–36	80	120
9	MeO	*76n*	23–24	85	120
10	MeO	*76o*	oil	71	120
3	CN	*76p*	114	16	121
4	CN	*76q*	108	18	121
5	CN	*76r*	166	34	121
6	CN	*76s*	163	11	121
7	CN	*76t*	112	5	121
8	CN	*76u*	84	24	121
9	CN	*76v*	68	12.5	121
10	CN	*76w*	46	3	121
3	NO_2	*76x*	145–148	4	122
4	NO_2	*76y*	102	45	122
5	NO_2	*76z*	97	21	122
6	NO_2	*77a*	116	42	122
7	NO_2	*77b*	94	20	122
8	NO_2	*77c*	80	48	122
9	NO_2	*77d*	41–43	13	122
10	NO_2	*77e*	78–90	2	122
4	NH_2	*77f*	94–95	39	119
5	NH_2	*77g*	76–77	56	119
6	NH_2	*77h*	79–80	67	119
7	NH_2	*77i*	77–78	60	119
8	NH_2	*77j*	42–44	55	119
9	NH_2	*77k*	−16	73	119
6	NHCOMe	*77l*	161–164	60	119
8	NHCOMe	*77m*	110	98	119
9	NHCOMe	*77n*	90–91	89	119
8	$N(COMe)_2$	*77o*	126	94	119
9	$N(COMe)_2$	*77p*	110–111	96	119
6	COOMe	*77q*	102–103	30	122
8	COOMe	*77r*	80–82	34	122

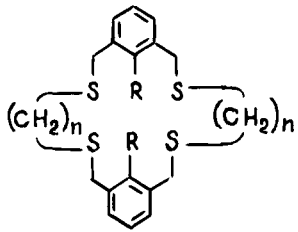
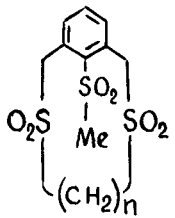
TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
	9	COOMe	*77s*	oil	39	122
	10	COOMe	*77t*	oil	57	122
	11	COOMe	*77u*	oil	46	122
	12	COOMe	*77v*	oil	49	122
	4	SMe	*77w*	100–103	3	122
	6	SMe	*77x*	101–104	15	122
	8	SMe	*77y*	oil	44	122
	9	SMe	*77z*	oil	53	122
	10	SMe	*78a*	oil	38	122
	4	SOMe	*78b*	154–156	29	123
	6	SOMe	*78c*	148–150	38	123
	8	SOMe	*78d*	128–130	19	123
	9	SOMe	*78e*	124–125	37	123
	10	SOMe	*78f*	112–114	22	123
	11	SOMe	*78g*	97–100	11	123
	4	SO_2Me	*78h*	144–147	5	122
	6	SO_2Me	*78i*	118–120	29	122
	8	SO_2Me	*78j*	177–180	11	122
	10	SO_2Me	*78k*	154–156	10	122
	11	SO_2Me	*78l*	128–130	19	122
	12	SO_2Me	*78m*	80–82	18	122
	2	Me	*78n*		12	116
	3	Me	*78o*	71–72	90	120
	4	Me	*78p*	48–49	65	120
	5	Me	*78q*	70–71	82	120
	6	Me	*78r*	93–94	81	120
	7	Me	*78s*	93–95	75	120
	8	Me	*78t*	74–76	96	120
	9	Me	*78u*	36–38	68	120



10	Me Me	*78v*	oil	72	120
4	Ph	*78w*	133–134	22	122
5	Ph	*78x*	109–110	23	122
6	Ph	*78y*	126–127	9	122
7	Ph	*78z*	oil	22	122
8	Ph	*79a*	62–64	18	122
10	Ph	*79b*	44–46	11	122
12	Ph	*79c*	oil	11	122
	R = F, X = CH_2OCH_2	*80a*	89–91	44	125
	R = F, X = CH_2SCH_2	*80b*	113–115	51	125
	R = Cl, X = $(CH_2OCH_2)_2$	*80c*	58–59	45	125
	R = Cl, X = $CH_2CH_2SCH_2CH_2$	*80d*	64–66	33	125
	R = Cl, X = $(CH_2SCH_2)_2$	*80e*	67–69	38	125
	R = I, X = *m*-C_6H_4	*80f*	160–162	35	119
	R = OH, X = *m*-C_6H_4	*80g*	119–120	24	119
	R = NO_2, X = CH_2OCH_2	*80h*	126–127	47	125
	R = NO_2, X = $(CH_2OCH_2)_2$	*80i*	82–83	31	125
	R = NO_2, X = $(CH_2SCH_2)_2$	*80j*	118–120	55	125
	R = NO_2, X = *m*-C_6H_4	*80k*	166–168	51	122
	R = NH_2, X = CH_2OCH_2	*80l*	88–89	74	125
	R = NH_2, X = $(CH_2OCH_2)_2$	*80m*	73–74	40	125
	R = NH_2, X = CH_2SCH_2	*80n*	138–140	77	119
	R = NH_2, X = $(CH_2OCH_2)_3$	*80o*	143–145	42	125
	R = NH_2, X = *m*-C_6H_4	*80p*	167–169	72	119
	R = NH_2, X = *p*-C_6H_4	*80q*	219–222 (subl)	90	119
	R = N=CHPh, X = *m*-C_6H_4	*80r*	183–185	96	119
	R = N=$CHC_6H_4OH(o)$, X = *m*-C_6H_4	*80s*	143–145	73	119
	R = $NHS(O_2)C_6H_4Me(p)$ X = *m*-C_6H_4	*80t*	249–250	81	119
	R = NHC(O)Me, X = *m*-C_6H_4	*80u*	162–165 (subl)	100	119
	R = OC(O)Me, X = *m*-C_6H_4	*80v*	177–179	39	119
	R = CO_2H, X = *m*-C_6H_4	*80w*	224–225	24	122
	R = CO_2Me, X = *m*-C_6H_4	*80x*	124–126	25	122
	R = CO_2CHMe_2, X = *m*-C_6H_4	*80y*	118–119	25	122
	R = CO_2CMe_3, X = *m*-C_6H_4	*81a*	154–155	35	122
	R = SMe, X = *m*-C_6H_4	*81b*	177–180	7	122

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
		R = SOMe, X = CH_2OCH_2	*81c*	194–196	27	123
		R = SOMe, X = CH_2SCH_2	*81d*	170–173	14	123
		R = SOMe, X = $(CH_2SCH_2)_2$	*81e*	155–156	22	123
		R = SOMe, X = *m*-C_6H_4	*81f*	245–247	25	123
		R = SOMe, X = *p*-C_6H_4	*81g*	189–191	13	123
		R = SO_2Me, X = *m*-C_6H_4	*81h*	202–204	20	122
		R = Ph, X = *m*-C_6H_4	*81i*	134	17	122
	2	H	*82a*	170–171	15	116
	2	F	*82b*	154–155	24	116
	2	Cl	*82c*	160–161	30	116
	2	Br	*82d*	176–177	20	116
	2	NO_2	*82e*	179–184	12	122
	2	NH_2	*82f*	215–217	49	119
	2	SMe	*82g*	170–173	5	122
	2	Ph	*82h*	217–218	5	122
	3	H	*82i*	116–117	19	116
	3	F	*82j*	142–143	13	116
	3	NO_2	*82k*	124	18	122
	3	NH_2	*82l*	113–114	88	119
	3	Ph	*82m*	236–237	7	122
	6	SO_2Me	*82n*	99–102	10	122
	4		*83a*	316(dec.)	39	122
	6		*83b*	340(dec.)	61	122
	8		*83c*	248–251	59	122
	10		*83d*	227–229	81	122
	11		*83e*	220–223	55	122
	12		*83f*	215–217	63	122

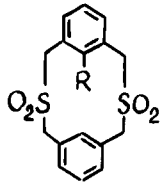
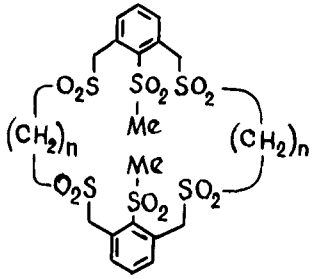
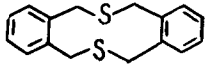
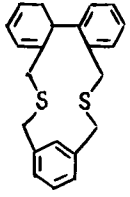
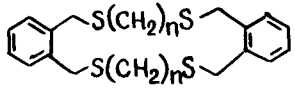
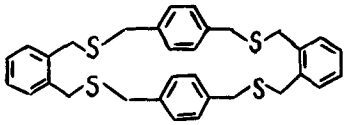
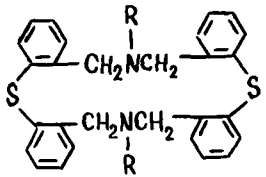
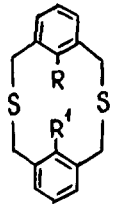
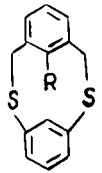
	OH	*84a*	330	81	119
	NO_2	*84b*	280(dec.)	97	122
	SO_2Me	*84c*	360(dec.)	56	122
		*85*	342(dec.)	31	122
		*86*	234–236	50	128,131
		*87*	150–152	50	131
	1	*88a*	198–200	3	131
	2	*88b*	142–144	5	131
	3	*88c*	208–210	5	131

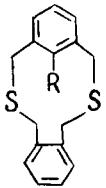
TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
			*89*	183–184	10	131
		Me	*90a*	290–291	25	132
		CH_2Me	*90b*	234–236	8	132
		CH_2CH_2Me	*90c*	232–234	9	132
		$CH_2CH{=}CH_2$	*90d*	234–236	11	132
		CH_2Ph	*90e*	170–172	3	132
		CH_2CH_2OH	*90f*	224–226	4	132
		$CH_2CH_2CH_2OH$	*90g*	238–240	27	132
		R = R^1 = H	*91a*	120–121	41	136
		R = H, R^1 = F	*91b*	149–150		134
		R = H, R^1 = Cl	*91c*	144–145		134
		R = H, R^1 = Br	*91d*	169–171		134
		R = H, R^1 = CN	*91e*	176–177	7	135
		R = H, R^1 = Me	*91f*	100–102	64	120
		R = H, R^1 = OMe	*91g*	157–158	51	120
		R = R^1 = F	*91h*	199–200	37	137
		R = R^1 = Cl	*91i*	270–274		134
		R = R^1 = Br	*91j*	259–262		134
		R = Cl, R^1 = F	*91k*	196		134
		R = R^1 = CN	*91l*	260	4	135
		R = Me, R^1 = F	*91m*	196–198	17	120
		R = Me, R^1 = Cl	*91n*	274–277	8	120
		R = Me, R^1 = Br	*91o*	232–236	8	120
		R = R^1 = Me	*91p*	240–250	12	120
		R = Me, R^1 = OMe	*91q*	229–231	32	120

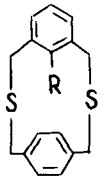
R = OMe, R^1 = F	*91r*	213–214	29	120
R = OMe, R^1 = Cl	*91s*	254–261	4	120
R = OMe, R^1 = Br	*91t*	274–279	2	120
R = R^1 = OMe	*91u*	248–250	8	120
R = Me, R^1 = *n*-Bu	*91v*	98–100	80	139
R = Me, R^1 = $CH_2CH_2CH{=}CH_2$	*91w*	189–190	55	140
R = Me, R^1 = CH_2CH_2OMe	*91x*	176–179	53	140



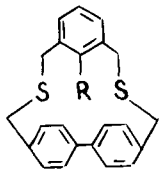
H	*92a*	145–146	21	143
F	*92b*	142–143	19	143
Cl	*92c*	176–177	15	143
Br	*92d*	217–218	30	143
CN	*92e*	216–217	24	135
Me	*92f*	140	81	120
OMe	*92g*	182	53	120



H	*93a*	157–158	18	143
F	*93b*	172–173	14	143
Cl	*93c*	232–233		118
Br	*93d*	225–226		118
Me	*93e*	202	59	120,137

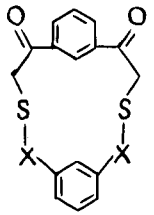
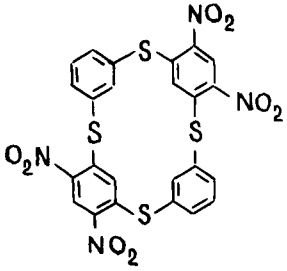
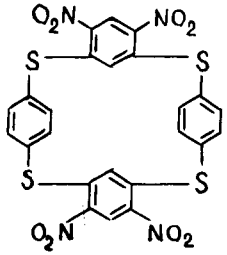


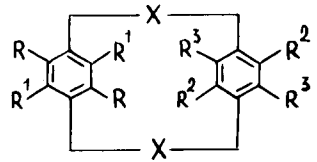
H	*94a*	172–173	13	116
F	*94b*	131–132	22	116
Cl	*94c*	115–116	18	116
CN	*94d*	104–105	10	116
Me	*94e*	112	65	120
OMe	*94f*	148	44	*120*



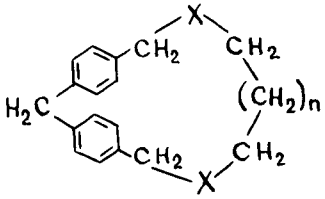
H	*95a*	125–126		118
F	*95b*	114–115		118
Cl	*95c*	124–125		118
Br	*95d*	141–142		118
Me	*95e*	107–109	41	118

TABLE 2 (*Continued*)

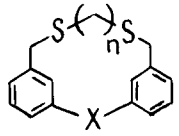
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
		bond	*96a*	218–219	21	144
		CH_2	*95b*	181–182	10	144
		$COCH_2$	*96c*	258–260	5	144
			*97*	>350	70	145
			*98*	350	70	145



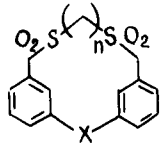
	$X = S$, $R = R^1 = R^2 = R^3 = H$	*99a*	183–184	25–30	147
	$X = S$, $R = Br$, $R^1 = R^2 = OMe$, $R^3 = H$	*99b*	235–237	7–15	146
	$X = S$, $R = R^2 = H$, $R^1 = CN$, $R^3 = OMe$	*99c*	276–277		147
	$X = S$, $R = R^3 = H$ $R^1 = CN$, $R^2 = OMe$	*99d*	306		147
	$X = SO_2$, $R = R^1 = R^2 = R^3 = H$	*99e*	>400	95	147
	$X = SO_2$, $R = R^2 = H$, $R^1 = CN$, $R^3 = OMe$	*99f*	270(dec.)	75	147
	$X = SO_2$, $R = R^3 = H$, $R^1 = CN$, $R^2 = OMe$	*99g*	270(dec.)		147



1	S	*100a*	179–180	20	148
2	S	*100b*	161	32	148
3	S	*100c*	123–130	55	148
1	SO_2	*100d*	290(dec.)	82	148
2	SO_2	*100e*	299–300 (dec.)		
3	SO_2	*100f*	281–283	79	148

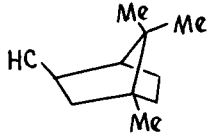
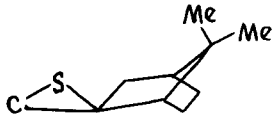
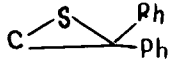
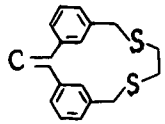
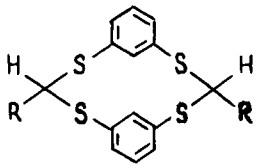


1	CH_2	*101a*	99–100	20	151
1	CO	*101b*	197–198	44	151
2	CH_2	*101c*	144–145	69	151
2	CO	*101d*	152–154	62	151
2	$C{=}NNH_2$	*101e*	210(dec.)	74	151



1	CH_2	*102a*	308–311 (dec.)	67	151
1	CO	*102b*	360(dec.)	86	151
2	CH_2	*102c*	325(dec.)	90	151
2	CO	*102d*	300(dec.)	89	151
3	CO	*102e*	300(dec.)	85	151
2	$CHOCMe_3$	*102f*	139–142	52	152
2	$C{=}NCMe_3$	*102g*	179–184	14	152
2	$C{=}N{=}N$	*102h*	131–133	14.5	152

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
	2		*102i*	270(dec.)	74	152
	2		*102j*	161–163	86	152
	2		*102k*	177–179	39	152
	2		*102l*	288–290	38	152
	2		*102m*	340	47	152
		H	*103a*	145–147	30	160
		Me	*103b*	183–188	12	160
		Ph	*103c*	224–226	45	160

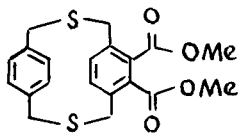
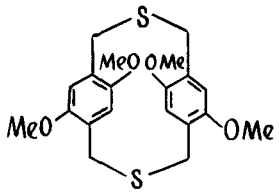
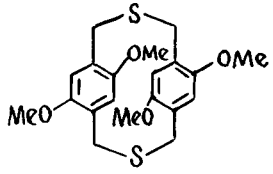
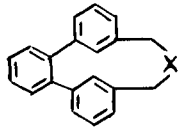
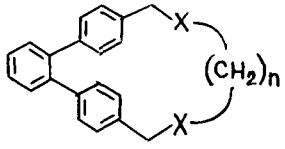
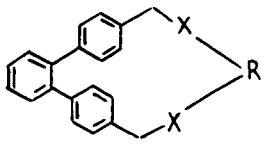
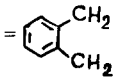
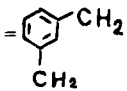
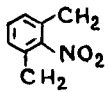
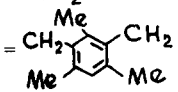
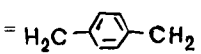
			*104*	174	30	161
			*105*	211–213		162
			*106*	243–246		162
		S	*107a*	146–147	28	153
		SO_2	*107b*	259	89	153
	2	S	*108a*	150–153	15	149,150
	3	S	*108b*	132–134	15	149,150
	4	S	*108c*	145–147	24	149,150
	5	S	*108d*	139–140	22	149,150
	6	S	*108e*	135–136	24	149,150
	7	S	*108f*	118–119	23	150
	8	S	*108g*	127–129	23	150
	9	S	*108h*	101–103	13	150
	10	S	*108i*	89–92	11	150
	2	SO_2	*108j*	360(dec.)	77	149,150

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
	3	SO_2	*108k*	295–297	86	150
	4	SO_2	*108l*	325–327	71	149,150
	5	SO_2	*108m*	262–264	86	149,150
	6	SO_2	*108n*	272–275	85	149,150
	7	SO_2	*108o*	325–326	86	150
	8	SO_2	*108p*	271–273	81	150
	9	SO_2	*108q*	239–242	74	150
	10	SO_2	*108r*	253–255	76	150
		X = S, R = $(CH_2CH_2)_2O$	*109a*	157–159	14	150
		X = S, R = $CH_2CH_2(OCH_2CH_2)_2$	*109b*	117–118	19	150
		X = S, R = $CH_2CH_2(OCH_2CH_2)_3$	*109c*	110–112	7	150
		X = S, R = $(CH_2CH_2)_2S$	*109d*	110–111	9	150
		X = S, R = 	*109e*	192–195	12	150
		X = S, R = 	*109f*	175–177	17	150
		X = S, R = 	*109g*	190–193	9	150
		X = S, R = 	*109h*	241–242	19	150
		X = S, R = 	*109i*	172–175	17	150

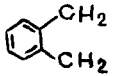
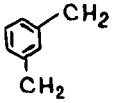
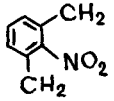
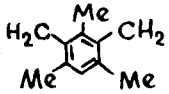
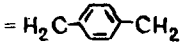
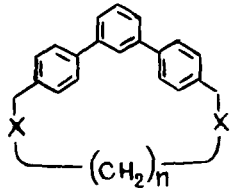
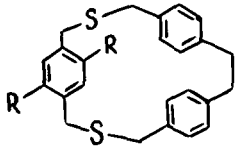
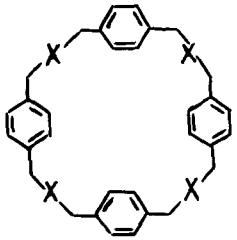
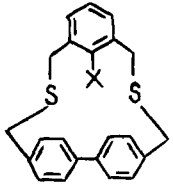
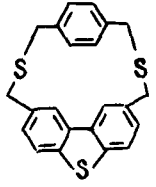
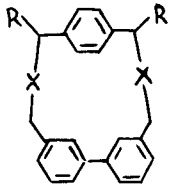
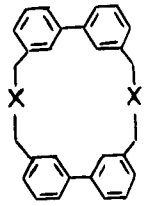
$X = S$, $R = (CH_2CH_2)_2O$		*109j*	297–299	90	150
$X = SO_2$, $R = CH_2CH_2(OCH_2CH_2)_2$		*109k*	232–234	60	150
$X = SO_2$, $R = CH_2CH_2(OCH_2CH_2)_3$		*109l*	235–238	87	150
$X = SO_2$, $R = (CH_2CH_2)_2SO_2$		*109m*	330–332 (dec.)	80	150
$X = SO_2$, R = 		*109n*	355 (dec.)	80	150
$X = SO_2$, R = 		*109o*	323–324	73	150
$X = SO_2$, R = 		*109p*	295 (dec.)	74	150
$X = SO_2$, R = 		*109q*	350 (dec.)	80	150
$X = SO_2$, R = 		*109r*	337–338	82	150
	10	S	*110a*	149–151	26	150
	11	S	*110b*	111–113	11	150
	10	SO_2	*110c*	315–317	89	150
	11	SO_2	*110d*	294–296	65	150
		H	*111a*	162–162.5	55	163
		F	*111b*	131–131.9	18	163
		Cl	*111c*	113–113.5	37	163
		Me	*111d*	143.2– −143.5	23	163
		OMe	*111e*	163–163.5	15	163

TABLE 2 (*Continued*)

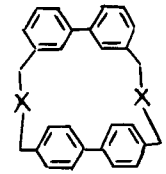
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
		S	*112a*	199–200		164
		$\overset{+}{S}Me \cdot BF_4^-$	*112b*	164–166		165
		H	*113a*	125–126		118
		F	*113b*	114–115		118
		Cl	*113c*	124–125		118
		Br	*113d*	141–142		118
		Me	*113e*	107–109	41	118
			*114*	260–261	88	



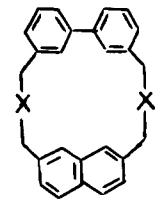
X = S, R = H	*115a*	213–215	49	168
X = SO_2, R = H	*115b*	>300	100	168
X = S, R = Me	*115c*	180–181	63	168



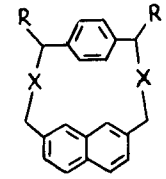
S	*116a*	266–268	74	169
$\overset{+}{S}Me \cdot BF_4^-$	*116b*	>300		169
SO_2	*116c*	>300	84	169



S	*117a*	249–251	73	167
$\overset{+}{S}Me \cdot BF_4^-$	*117b*	205–207 (dec.)	100	167
SO_2	*117c*	>320	95	167

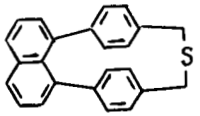
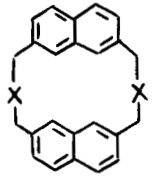
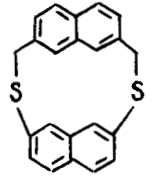
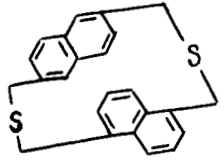


S	*118a*	234–235	49	170,171
$\overset{+}{S}Me \cdot BF_4^-$	*118b*	>300		170,171
SO_2	*118c*	>350		170



X = S, R = H	*119a*	239–241	50	172,173
X = S, R = Me	*119b*	245–246	55	172,173
X = $\overset{+}{S}Me \cdot BF_4^-$, R = H	*119c*	>340	100	172.173
X = $\overset{+}{S}Me \cdot BF_4^-$, R = Me	*119d*	>360	100	172,173
X = SO_2, R = H	*119e*	>340	97	172

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
			*120*			174,175
		S	*121a*	240–244		176,177
		$\overset{+}{S}Me \cdot BF_4^-$	*121b*	>210		176
		SO_2	*121c*	>300		176
			*122*	228–230	40	178
			*123*	281–283	6	179

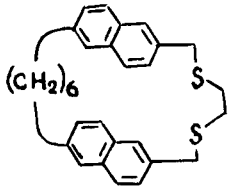
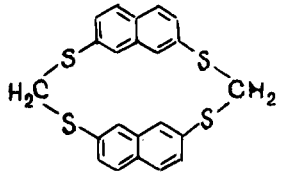
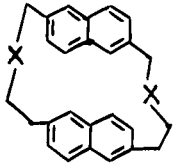
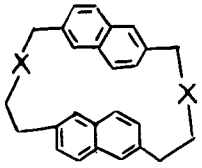
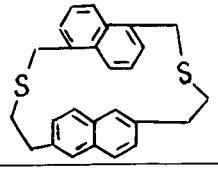
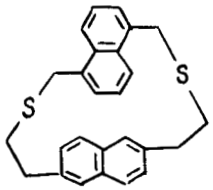
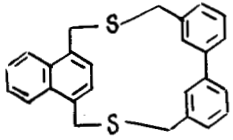
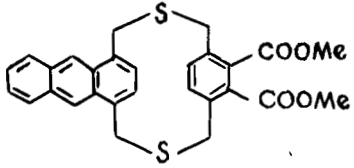
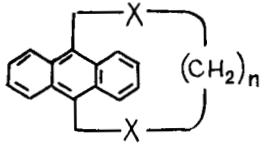
		*124*	190–192	56	180
		*125*			181
	S SO_2	*126a* *126b*			182 182
	S SO_2	*127a* *127b*			182 182
		*128*			182

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
			*129*			182
			*130*	192–193	46	163
			*131*	131	31	161
	8	S	*132a*	158–160	29	183
	12	S	*132b*	108–109	24	183
	8	SO_2	*132c*	320–322	70–90	183
	12	SO_2	*132d*	227–229	61–80	183

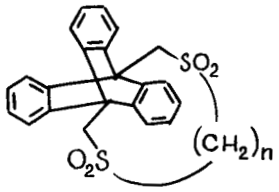
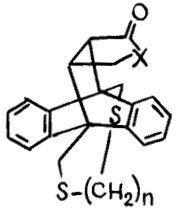
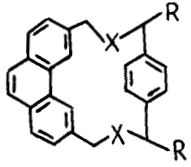
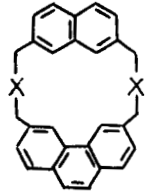
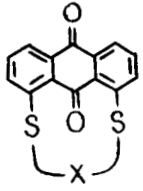
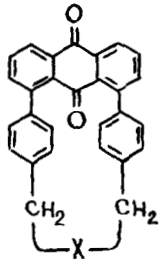
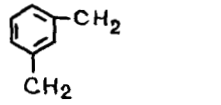
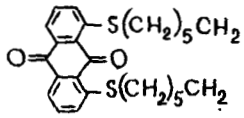
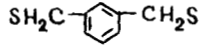
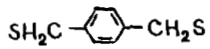
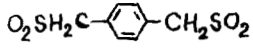
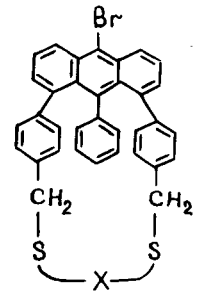
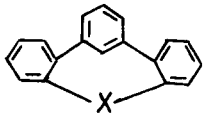
	8		*133a*	>350	4	183
	12		*133b*	368–370	5	183
	8	O	*134a*	198–200	2	183
	12	O	*134b*	202–204	53	183
	8	NPh	*134c*	188–190	4	183
	12	NPh	*134d*	199	35	183
		X = S, R = H	*135a*	248–250	52	184,185
		X = $\overset{+}{S}MeBF_4^-$, R = H	*135b*	>300	100	185
		X = SO_2, R = H	*135c*	>300	26	185
		X = S, R = Me	*135d*	208–210	36	185
		X = $\overset{+}{S}MeBF_4^-$, R = Me	*135e*	300(dec.)	90	185
		S	*136a*	249–250	60	186
		$\overset{+}{S}Me \cdot BF_4^-$	*136b*	300	94	186
		$CH_2(CH_2)_7CH_2$	*137a*	187	2	187
		$CH_2(CH_2)_8CH_2$	*137b*	209	3	187
		$CH_2CH_2(OCH_2CH_2)_3$	*137c*	143	8	187

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
			*137d*	186	2	187
			*137e*	310	4	187
		S	*138a*	294–296	22	188
		SO_2	*138b*	>350	66	188
		SCH_2CH_2S	*138c*	273–275	28	188
		$SO_2CH_2CH_2SO_2$	*138d*	>350	91	188
			*138e*	253–254	33	188
			*138f*	>350	86	188
			*138g*			188
			*138h*	>350	93	188





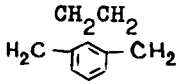
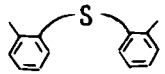
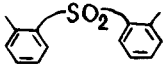
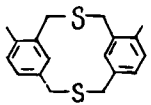
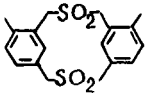
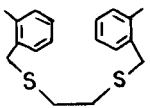
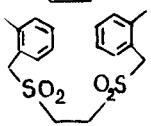
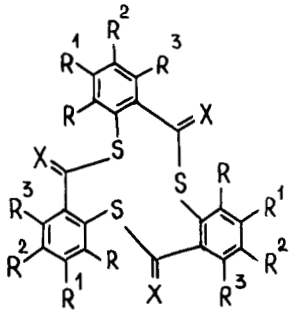
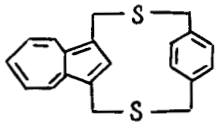
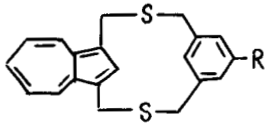
	*139a*	205–207	24	188
	139b	208–210	27	188
	*140a*	273–274	19	189
	*140b*	297	70	189
	*140c*	295	7	189
	*140d*	>370	64	189
	*140e*	212	45	189
	*140f*	235–240	66	189

TABLE 2 (*Continued*)

Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
		X = H, R = R¹ = R² = R³ = H	*141a*	197–198	6.4	190,191
		X = O, R = Me, R¹ = R² = R³ = H	*141b*	300–302	7	192
		X = O, R² = Me, R = R¹ = R³ = H	*141c*	250–255	10	192
		X = O, R³ = Me, R = R¹ = R² = H	*141d*	>300	8	192
		X = O, R = R³ = Me, R¹ = R² = H	*141e*	>300	7	192
			*142*	168(dec.)	40	194
		H	*143*			195
		Me	*144*			195

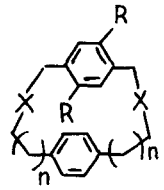
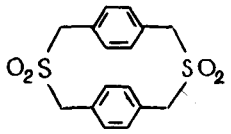
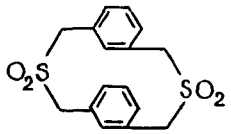
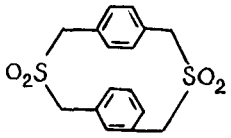
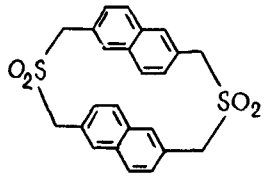
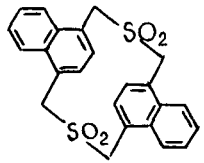
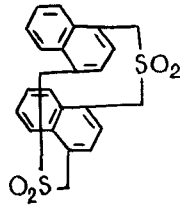
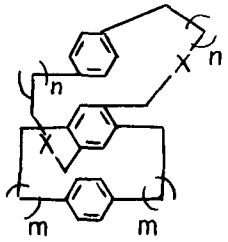
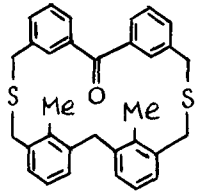
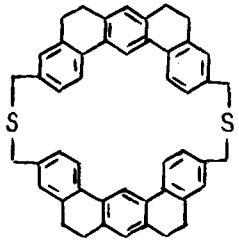
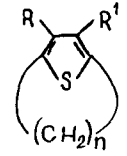
	1	X = S, R = H	*145a*	184–185	25–30	201
	1	X = SO_2, R = H	*145b*	400	95	200,201
	1	X = S, R = Br	*145c*	181.5–182.5	62	202
	1	X = S, R = CN	*145d*	259.5–261.5	68	202
	1	X = SO_2, R = CN	*145e*		82	202
	2	X = S, R = Br	*145f*	137–138	87	202
	2	X = S, R = CN	*145g*	164–165	53	202
	2	X = SO_2, R = CN	*145h*		96	202
			*146*	250(dec.)	97	200
			*147*	350	88	200
			*148*	300	92	200
			*149*	350	95	200
			*150*	300	92	200

TABLE 2 (*Continued*)

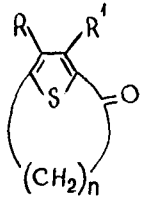
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
			*151*	300	65	200
	m = n = 1	S	*152a*	156.5–158	25	202
	m = 2, n = 1	S	*152b*	204–205	63	202
	m = 3, n = 0	S	*152c*	206.5–208	88	202
	m = 3, n = 1	S	*152d*	280–282	77	202
	m = 3, n = 2	S	*152e*	120–122	67	202
	m = 3, n = 2	SO_2	*152f*		58	202
			*153*	297–299	80	204



		154	291	55	205

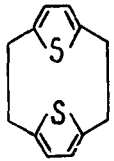
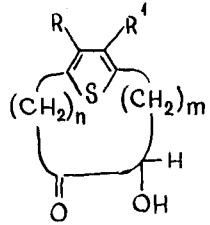
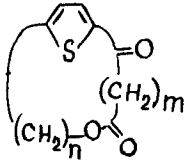


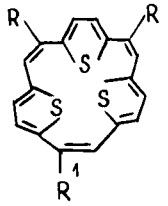
8	R = R¹ = H	*155a*	[80–81(15.0)]	210–212
10	R = R¹ = H	*155b*	[67.5(0.03)]	212,226
10	R = R¹ = Ac	*155c*	59–60.5	212,237
11	R = H, R¹ = Br	*155d*	45–46	



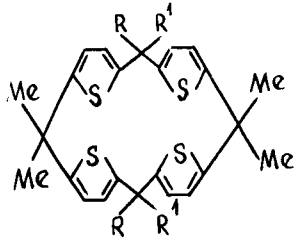
8	R = R¹ = H	*156a*		211,231, 233,240
9	R = R¹ = H	*156b*	35.5–37.5	206,210, 212,231, 217,233, 239,240
9	R = Me, R¹ = H	*156c*	58.5–60	206,230
9	R = H, R¹ = Me	*156d*	90–91.5	206,230
9	R = *i*-Pr, R¹ = H	*156e*	80.5–81.5	212,213,228
9	R = NO_2, R¹ = H	*156f*	89.5–90	212,226
10	R = R¹ = H	*156g*	45–45.2	211,224,225, 231,233,237, 239,240
10	R = Me,R¹ = H	*156h*	40.5–42	221,230
10	R = H, R¹ = Me	*156i*	76.5–78.5	221,230
10	R = H, R¹ = 2-CO_2Et	*156j*	[189–192(0.15)]	216–219,224, 225,229,232,240
11	R = R¹ = H	*156k*	31–32	211,231,233, 239,240

TABLE 2 (*Continued*)

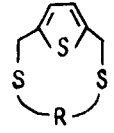
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
	12	R = R¹ = H	*156l*	[170–171(0.2)]		211,231,233, 239,240
			*156m*			328
	m = n = 4	R = R¹ = H	*157a*	69.5–71		223,226,240
	m = n = 4	R = R¹ = Me	*157b*	117–119		223,240
	m = 5, n = 4	R = R¹ = H	*157c*	62–64		223,240
	m = 2, n = 5		*158a*	67–68		206,207,222
	m = 2, n‡ = 5; 2,3-benzo		*158b*			237,243
	m = 3, n = 4		*158c*	113–114		243,206,207, 214,215
	m = 3, n = 5		*158d*	114–115		214
	m = 4, n = 3		*158e*	70–71		206,207,222, 237,243
	m = 5, n = 2		*158f*	134–135		222,257,243,
	m = 5, n = 4		*158g*			206,207
	m = 1, n = 6		*158h*			222

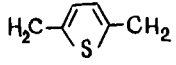


$R = R^1 = H$	*159a*	74.5–75.5	253,254
$R = CO_2H$, $R^1 = CO_2Me$	*159b*	dec.	253,254
$R = R^1 = CO_2Me$	*159c*	257–259	253,254
$R = R^1 = CO_2H$	*159d*	360	253,254

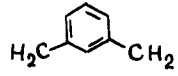


$R = R^1 = Me$	*160a*	338	255,256
$R = H$, $R^1 = OH$	*160b*	280 (dec.)	256,257
$R = Me$, $R^1 = OH$	*160c*	280 (dec.)	256,257

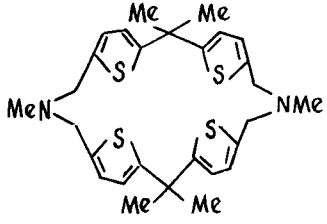




	161a	234(dec.)	258

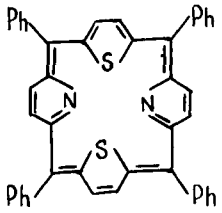
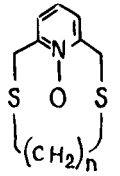
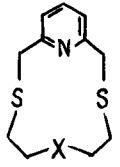
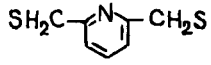


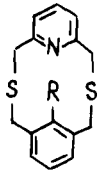
	161b	210	258



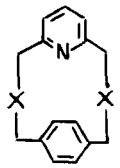
	162	168.5–170	220

TABLE 2 (*Continued*)

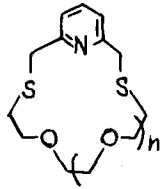
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
			*163*		10	259
	5		*164a*	147–148		262
	6		*164b*	138–140		262
	7		*164c*	89		262
	8		*164d*	73–75		262
	9		*164e*	117–120		262
	10		*164f*	54–55		262
		S	*165a*	162–163		263,264
		SO	*165b*	171–174		264,265
		SCH_2CH_2S	*165c*	131–133		263,264
		S-S	*165d*	151–153 (subl.)		264
		NMe	*165e*	67–69		264
			*165f*	213–216 (subl.)		264



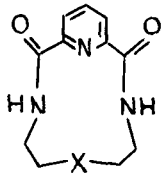
H	*166a*	173–175	266
Me	*166b*	135–136	267
F	*166c*	174–175	266
NO_2	*166d*	159–160	268



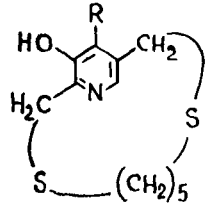
S	*167a*	177–178	269,270
$\overset{+}{S}Me\ BF_4^-$	*167b*		270
$N \rightarrow O$, SO_2	*167c*	340	270,271
$N \rightarrow O$, SO	*167d*	220–250	271



0	*168a*	133–135	272,273
1	*168b*	90–91	272,273
2	*168c*	58–59	272,273
3	*168d*		272

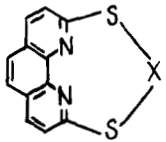
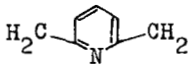
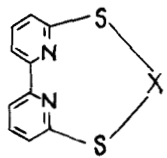
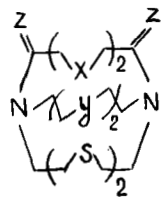


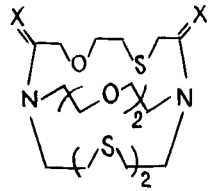
S	*169a*	242–243	264
S-S	*169b*	234–236	264



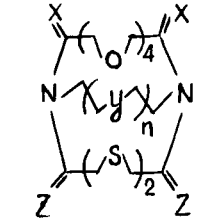
CH_2NH_2	*170a*		274
CHO	*170b*		274
CH=NOH	*170c*		274

TABLE 2 (*Continued*)

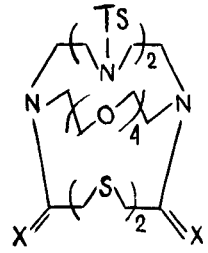
Compound	m, n	Substituents	Compd. No.	Mp. [bp (mm)], °C	Yield, %	Refs.
1	2	3	4	5	6	7
		$CH_2CH_2SCH_2CH_2$	*171a*			276
		$CH_2CH_2(OCH_2CH_2)_2$	*171b*			276
		$CH_2CH_2(SCH_2CH_2)_2$	*171c*			276
		$CH_2CH_2(OCH_2CH_2)_3$	*171d*			276
		$(CH_2)_6$	*171e*			276
		$(CH_2)_8$	*171f*			276
		m-$C_6H_4(CH_2)_2$	*171g*			276
			*171h*			276
		$(CH_2)_8$	*172a*			276
		$CH_2CH_2(OCH_2CH_2)_3$	*172b*			276
		X = Y = Z = O	*182a*	oil	50	293
		X = Y = O, Z = H_2	*182b*	78–80	85	293
		X = Z = O, Y = S	*182c*	oil	40	293
		X = O, Y = S, Z = H_2	*182d*	86–87	95	293
		X = Y = S, Z = O	*182e*	oil	20	293
		X = Y = S, Z = H_2	*182f*	172	80	293
		X = N-Ts, Y = Z = O	*182g*			293
		X = N-Ts, Y = O, Z = H_2	*182h*			293
		X = NH, Y = O, Z = H_2	*182i*			293
		X = N-Ts, Y = S, Z = O	*182j*			293
		X = N-Ts, Y = S, Z = H_2	*182k*			293
		X = NH, Y = S, Z = H_2	*182l*			293



	$X = O$	*183a*	oil	50	293
	$X = H_2$	*183b*	oil	95	293

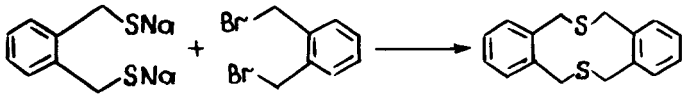


2	$X = O$, $Y = S$, $Z = H_2$	*184a*			293
2	$X = H_2$, $Y = S$, $Z = H_2$	*184b*			293
4	$X = H_2$, $Y = O$, $Z = O$	*185a*			293
4	$X = H_2$, $Y = O$, $Z = H_2$	*185b*			293
2	$X = O$, $Y = O$, $Z = H_2$	*186a*			293
2	$X = H_2$, $Y = O$, $Z = H_2$	*186b*			293



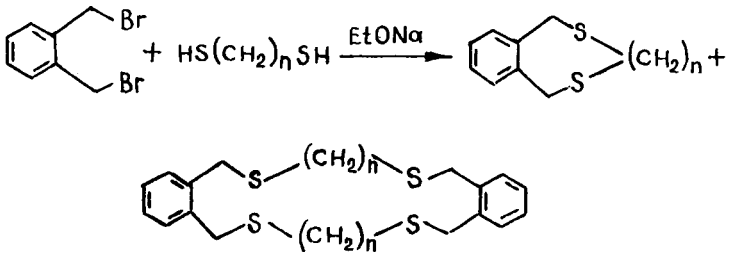
	$X = O$	*187a*			293
	$X = H_2$	*187b*			293

The 10-membered *o*-dithiacyclophane containing two benzene rings was synthesized in 1903 by reaction of *o*-dibromoxylene with the corresponding araliphatic sodium dithiolate.[128]



86

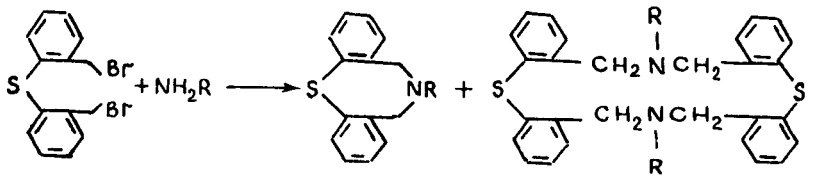
The cyclization of *o*-dibromoxylene with sodium α,ω-alkanedithiolates leads to monomeric *o*-dithiacyclophanes and dimeric tetrathiacyclophanes *88a–88c* and *89* in 3–10% yield.[129–131]



88a–88c

n = 1–3

Some 8-membered *o*-azathiacyclophanes and their 16-membered dimers *90a–90g* have been prepared by reaction of bis[2-(bromomethyl)phenyl] sulfide with primary amines.[132] These compounds have been oxidized to the corresponding sulfoxides and sulfones.[133]

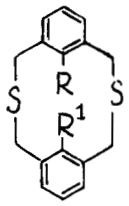


90a–90g

R = Me, CH_2Me, CH_2CH_2Me, $CH_2CH{=}CH_2$, CH_2Ph, CH_2CH_2OH, $CH_2CH_2CH_2OH$

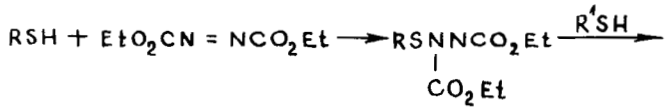
The synthesis of binuclear cyclophanes containing two different substituents in the benzene ring has been performed by reaction of 2,6-bis(bromomethyl) substituted benzenes with substituted *m*-bis(mercaptomethyl)benzenes (compounds *91a–91x*, Table 2).[120,134–142]

The addition of two thiol molecules to azodicarboxylic acid diethyl ester leads to a disulfide, the partial desulfurization of which with tris(*N*,*N*-diethylamino)phosphine affords the corresponding sulfide. This route gives the two dithia[3.3]-metacyclophanes *91a* and *91p* (Table II).[136]

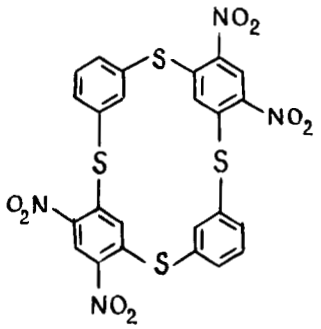


91a–91x

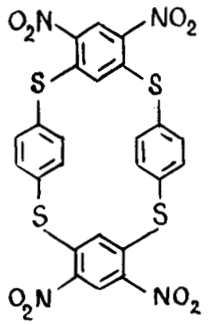
R = H, F, Cl, Br, CN, Me, OMe, R = H, F, Cl, Br, CN, Me, *n*-Bu, $CH_2CH_2CH{=}CH_2$, OMe, CH_2CH_2OMe



10-, 11-, 13-, and 15-membered dithiacyclophanes with intraannular substituents in the benzene ring have been synthesized by reaction of 2,6-bis(bromomethyl)benzenes with aromatic and aliphatic dithiols (*92a–95e*, Table 2). Another type of dithiametacyclophanes (*96a–98*) was also obtained:[144,145]

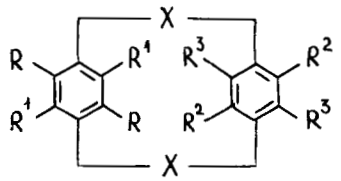


97



97a

The dithiaparacyclophanes *99a–99g* containing bromine atoms, methoxy, or nitrile groups in the positions 2 and 5 of the benzene rings were synthesized by reaction of

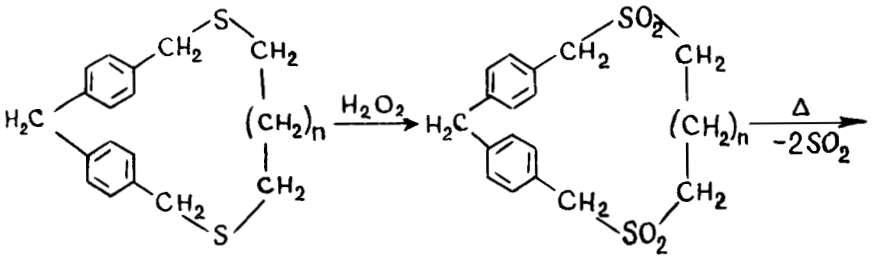


99a–99g

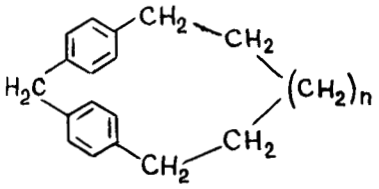
X = S, SO_2; R = H, Br; R^1 = H, OMe, CN; R^2 = H, OMe, R^3 = H, OMe

1,4-bis(mercaptomethyl) substituted benzenes with the corresponding 1,4-bis (bromomethyl) substituted benzenes.[146,147]

The pyrolysis of the corresponding cyclic sulfones according to the Scheme below has been widely applied recently for the synthesis of cyclophanes.



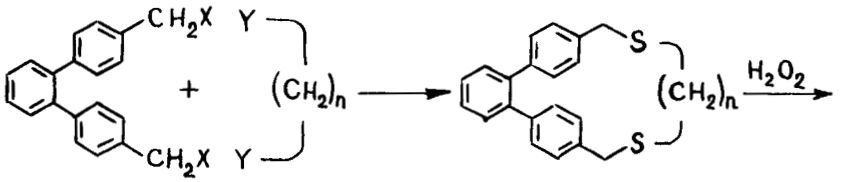
100a–100c 100d–100f



n = 1–3

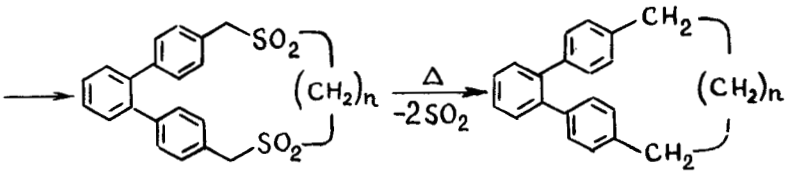
Sterically hindered paracyclophanes have been synthesized in this way.[148]

A number of cyclophanes possessing from two to four benzene rings in the molecule have been described. The main synthetic route to dithiacyclophanes the oxidation of which to disulfones and further pyrolysis leads to cyclophanes, is the



n = 2–10;
X = Br, SH; Y = SNa, Br

108a–108i

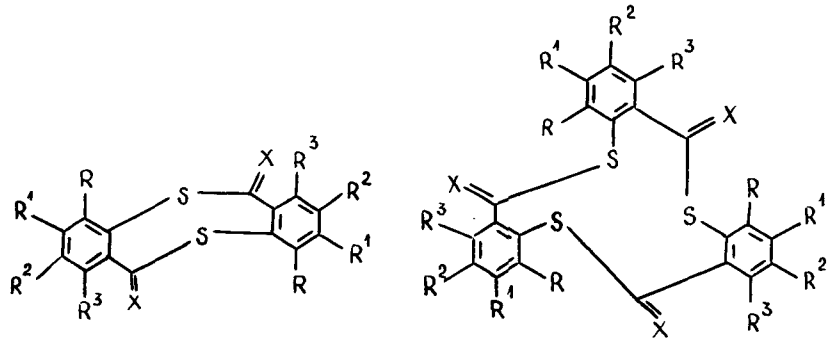


108j–108r

reaction of the corresponding dibromides with dithiols (compounds *101a–112b*, Table 2).[149–164]

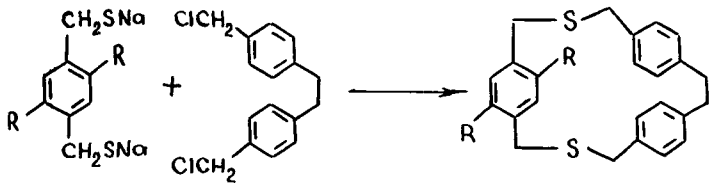
This method has been used for the preparation of dithiabiphenylophanes,[165–169] dithiabiphenylnaphthalenophanes,[170,171] dithianaphthalenophanes,[172–182] dithiaanthracenophanes, dithiaphenanthrenophanes,[161,183–185] and dithiaphenanthronaphthalenophanes[186] (*117a–136*, Table 2). Sulfur-containing anthraquinonophanes and pentaphenylenophanes have been reported.[187–189]

The homocyclization of *o*-chlorothiophenol by treatment with sodium hydroxide or that of *o*-mercaptobenzoic acid by treatment with P_4O_{10} at high dilution yields both medium-ring size dithiaorthocyclophanes and the macrocyclic trithiaorthocyclophanes *141a–141l*.[190–193]



X = H_2, R = R^1 = R^2 = R^3 = H **141a**
X = O, R = Me, R^1 = R^2 = R^3 = H **141b**
X = O, R = R^1 = R^3 = H, R^2 = Me **141c**
X = O, R = R^1 = R^2 = H, R^3 = Me **141d**
X = O, R = R^3 = Me, R^1 = R^2 = H **141e**

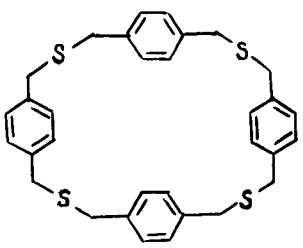
For the elucidation of the effects of inner rotation of macrocyclophane benzene rings the tricyclic dithiaparacyclophanes *111a–111e* containing different substituents in the positions 2 and 5 of the benzene ring have been obtained.[163]



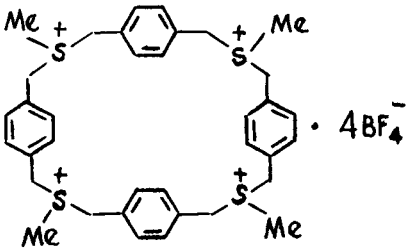
R = H, F, Cl, Me, OMe **111a–111e**

The synthesis is carried out by reaction of sodium dithiolates with 1,2-bis[4-(chloromethyl)-phenyl]ethane in a large amount of mixed solvent (benzene-ethanol). The yields of the dithiacyclophanes *111a–111e* are 15–55%.

Treatment of the tetrasulfide *112a* with $Me_3O^+BF_4^-$ gives the water-soluble tetrathiaparacyclophane *112b*.[164]

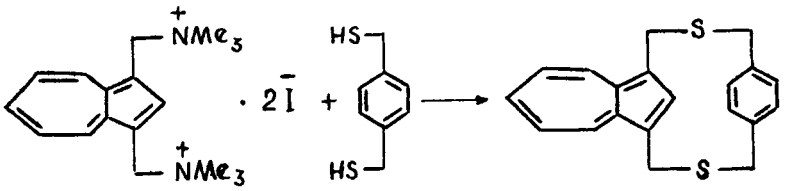


112a



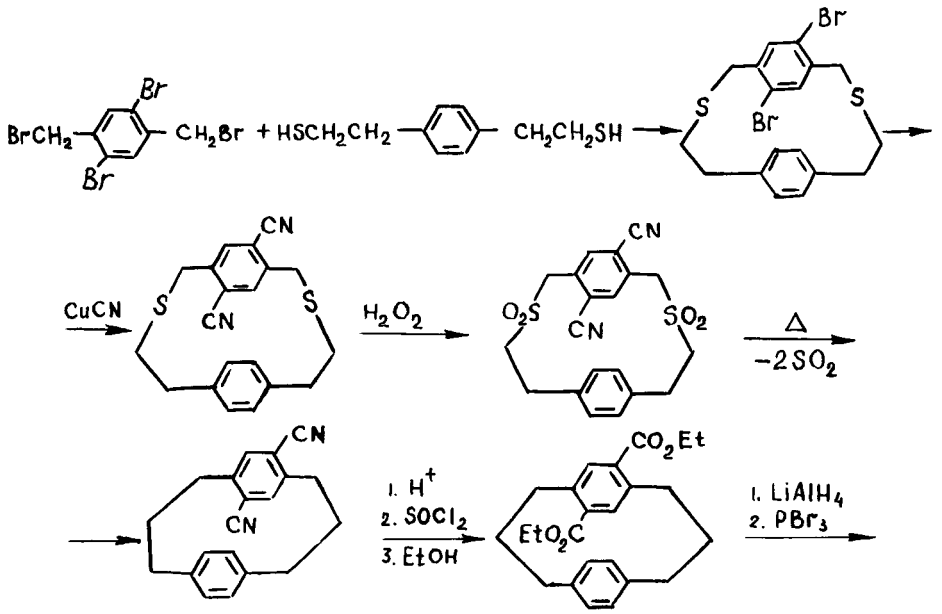
112b

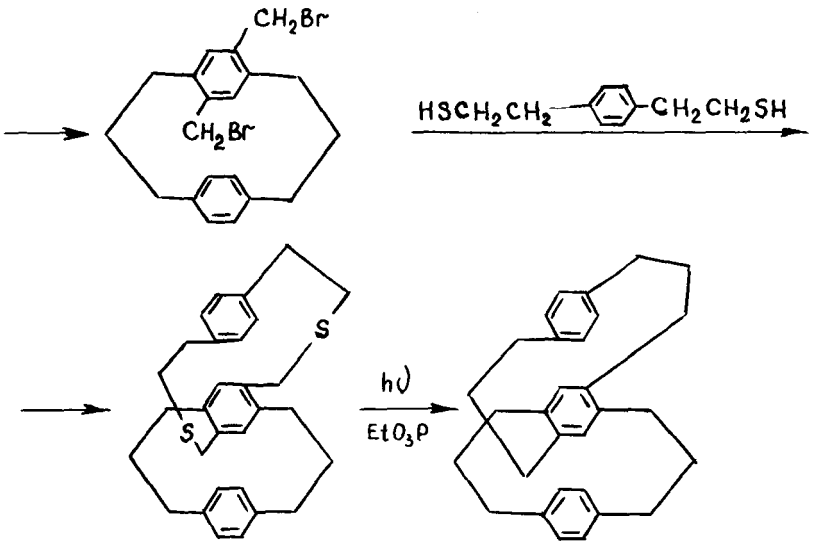
The technique of high dilution has allowed the dithiaazulenoparacyclophane *142* to be synthesized by reaction of 1,3-bis(trimethylammoniomethyl)azulene diiodide with 1,4-bis(mercaptomethyl)benzene.[194]



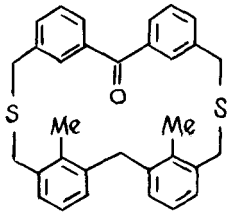
The dithiaazulenometacyclophanes *143* and *144* have also been obtained.[195]

Two- and three-layered cyclophanes have been prepared according to the Scheme below for the purpose of examination of transannular interactions between the benzene ring π-electrons.[196–203] The synthesis is based on the pyrolysis of bis-sulfones or photoextrusion of sulfur from dithiacyclophanes:



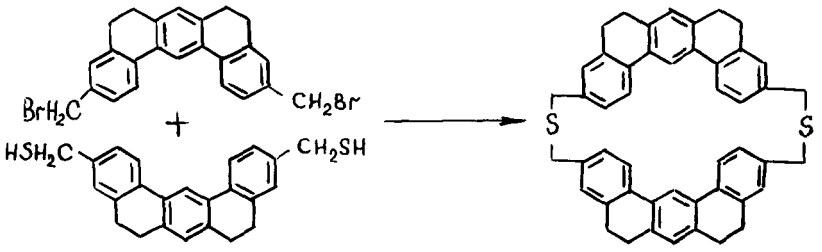


The dithiametacyclophane *153* has been prepared in 80% yield by cyclization of 3,3′-bis(bromomethyl)benzophenone with bis[3-(mercaptomethyl)-2-methylphenyl]methane.[204]



153

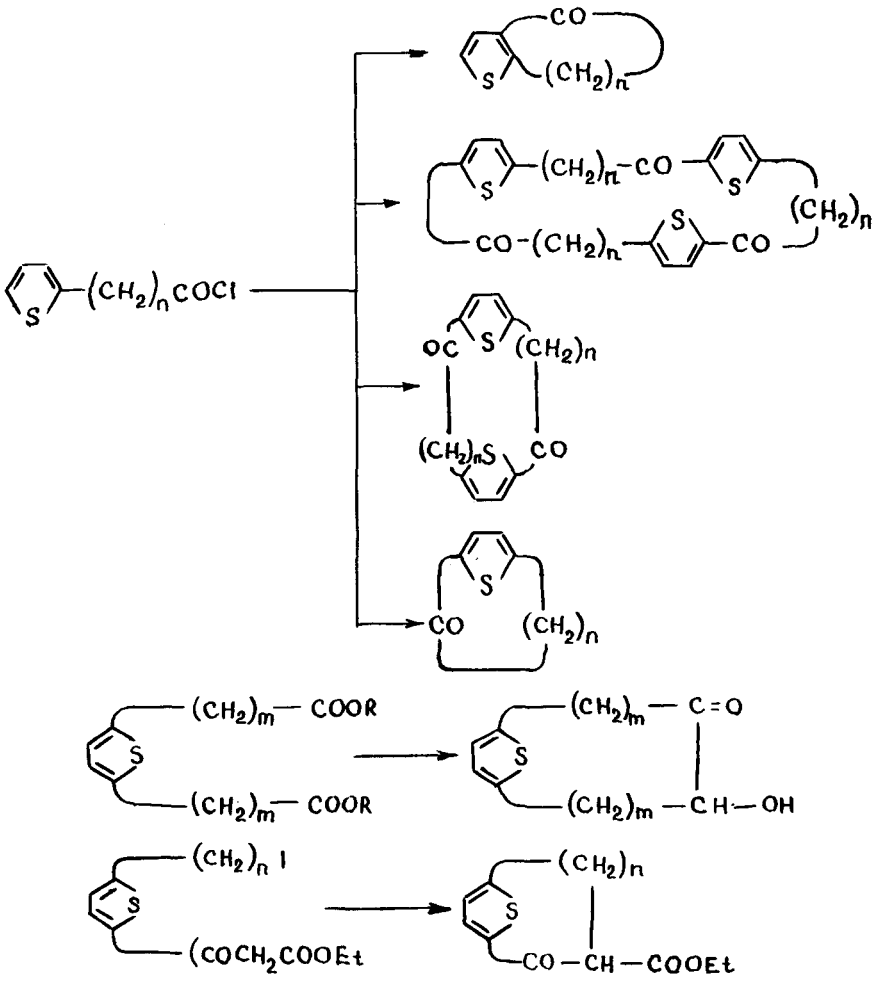
The synthesis of dithiadibenzoanthracenophane *154* in 55% yield by reaction of bis(bromomethyl)dibenzoanthracene with bis(mercaptomethyl)dibenzoanthracene has been reported.[205]



154

2.2. *Cyclothiophenophanes*

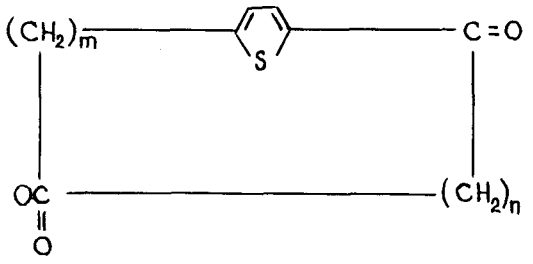
The synthesis of macrocyclic compounds containing one, two, or more thiophene rings is possible by intra- and intermolecular acylation of ω-thienylakanecarboxylic acid chlorides, acyloin condensation of 2,5-bis(carbalkoxyalkyl)-thiophenes, and by intramolecular alkylation of ω-haloalkyl substituted β-keto esters of the thiophene series.[206–244]



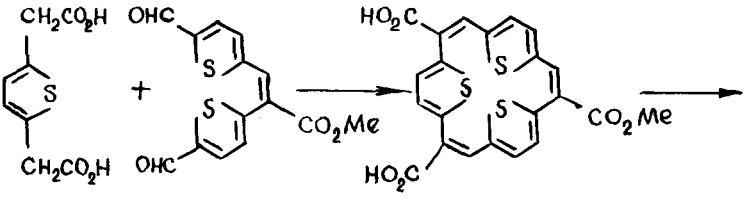
The melting points and yields of the compounds thus obtained are presented in Table 2 (*155a–158h*).

The X-ray determination of geometric and conformational parameters of isomeric ansa-ketolactones containing the thiophene ring has allowed the explanation of both the different ease of the formation of macrocyclic keto lactones depending on the

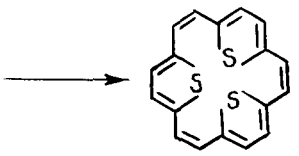
ester group position in the ansa bridge and the physical and chemical features of the above compounds.[245–252]



The trinuclear unsaturated thiophenophane *159*a has been prepared by Perkin cyclocondensation of 2,5-thiophenediacetic acid and methyl *cis*-α,β-bis(5-formyl-2-thienyl)acrylate.[253,254]



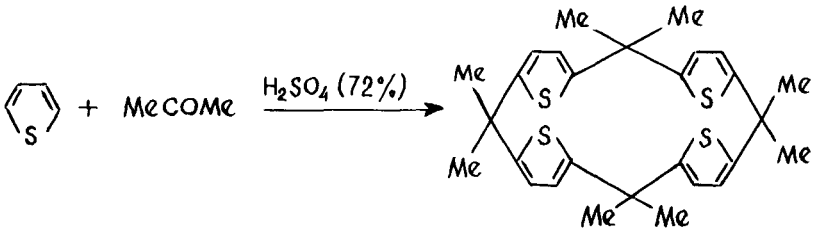
159b



159a

The diacid *159b* is converted to the triester *159c* which forms the triacid *159d* upon alkaline hydrolysis. The decarboxylation of the latter in the presence of copper chromite in quinoline at 210–220 °C gives the unsubstituted thiophenophane *159a*. The melting points and yields of compounds *159a–159d* are listed in Table 2.

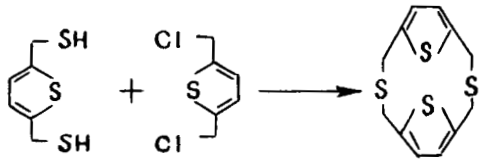
The reaction of thiophene with acetone in the presence of 72% sulfuric acid affords the macrocycle *160a* possessing four thiophene rings.[255]



160a

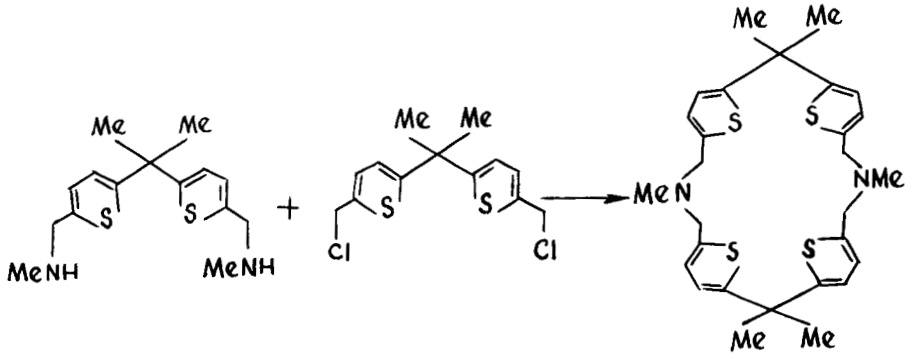
Its analogs *160b* and *160c* have been obtained by reaction of 2,2-bis-(5-lithio-2-thienyl)propane with 2,2-bis(5-formyl-2-thienyl)propane or 2,2-bis(5-acetyl-2-thienyl)propane.[256,257]

The dithiathiophenophanes *161a* and *161b* have been synthesized by cyclization of 2,5-(bis(mercaptomethyl)thiophene with 2,5-bis-(chloromethyl)thiophene or 1,3-bis(bromomethyl)benzene in high dilution.[258]



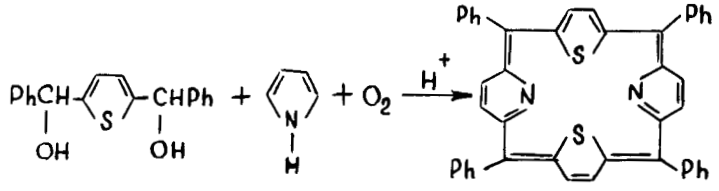
161a

The thiophenophane *162* containing amino groups as bridges, obtained by reaction of 2,2-bis(5-methylaminomethyl-2-thienyl)-propane with 2,2-bis(5-chloromethyl-2-thienyl)propane has also been reported.[220]



162

The reaction of pyrrole with 2,5-bis(α-hydroxybenzyl)thiophene affords tetraphenyl-21,23-dithiaporphyrine *163* in 10% yield.[259]

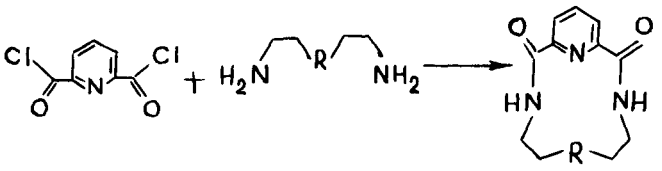


163

2.3. Sulfur-containing cyclopyridinophanes

The sulfur-containing cyclopyridinophanes *164a–168d* have been synthesized by cyclization of 2,6-bis(bromomethyl)pyridine with various α,ω-alkanedithiols (Table

2).[260–273] The cyclopyridinophanes *169a* and *169b* containing two amide groups have been obtained by reaction of 2,6-pyridinedicarboxylic acid dichloride with bis(aminoalkyl) sulfides.[264]

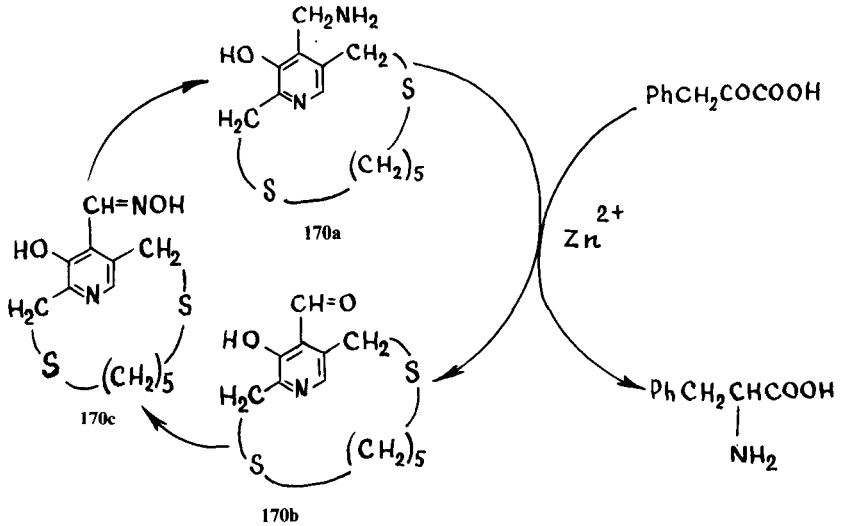


R = S, S—S

169a 169b

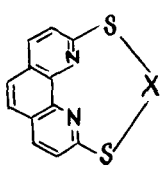
The above sulfur-containing cyclopyridinophanes form crystalline complexes with the transition metal ions Ag^{+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Pd^{2+}, Au^{3+}, and Pt^{4+} in 36–96% yield.

(-)-15-Aminomethyl-14-hydroxy-2,8-dithia[9](2,5)-cyclo-pyridinophane *170a* can be used as a transamination agent in the reaction with phenylpyrotartaric acid[274] and zinc salts as catalysts. The dithiapyridoxamine *170a* was obtained by treatment of the pyridinophane *170b* with NH_2OH-HCl-AcONa-EtOH, followed by reduction of the oxime *170c* formed with $NaBH_2S_3$ in THF. The transamination is performed by mixing dithiacyclopyridinophane *170a*, sodium phenylpyrotartrate and a zinc salt in acetonitrile at room temperature for 20 hours. The maximum yield of phenylalanine is 83%.

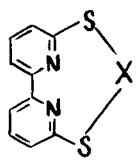


170a **170c** **170b**

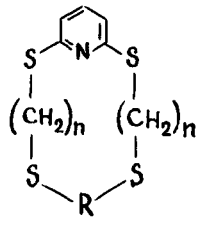
The dithiacyclophenanethrolinophanes and dithiacyclodipyridinophanes *171a–172b* (see Table 2) in which the pyridine rings are bridged by sulfur atom have been synthesized by reaction of 2,9-dichloro-1,10-phenanthroline or 6,6′-dichloro-2,2′-dipyridyl with sodium α,ω-dithiolates in 3-methyl-1-butanol.[276] These macroheterocycles do not form crystalline complexes with alkali and alkali earth metal ions. As far as heavy metals are concerned they form complexes with silver and mercury ions only.



171a–171h



172a, 172b



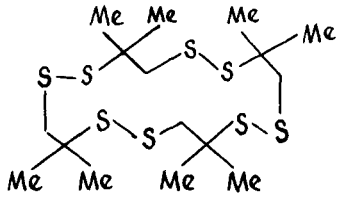
173a, 173b

n = 2; R = CH_2CH_2

The reaction of 2,6-dihalopyridines with sodium α,ω-dithiolates gives the dithiacyclopyridinophanes *173a* and *173b* in which the pyridine ring is bound to the polymethylene bridge via the sulfur atoms.[275]

3. *Macroheterocycles Containing Di- and Polysulfide Groups*

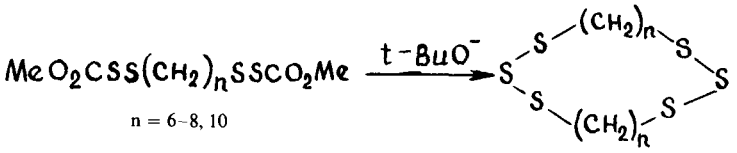
A 16-membered macrocyclic polydisulfide containing four disulfide groups has been synthesized by treatment of the product of the addition of disulfur dichloride to isobutene with alcoholic sodium hydrosulfide (comp. *174*).[277]



174

The same compound is obtained by reaction of sodium hydrosulfide with 2-chloro-2-methyl-1-propyl disulfide, methallyl disulfide, or sodium methallyl thiosulfate, the maximum yield of the macrocycle *174* being 45%.

The macroheterocycles *175a–175d* possessing two trisulfide fragments have been prepared by decomposition of α,ω-alkylene-bis(sulfenyl)-dithiocarbonates with sodium *t*-butoxide.[278]

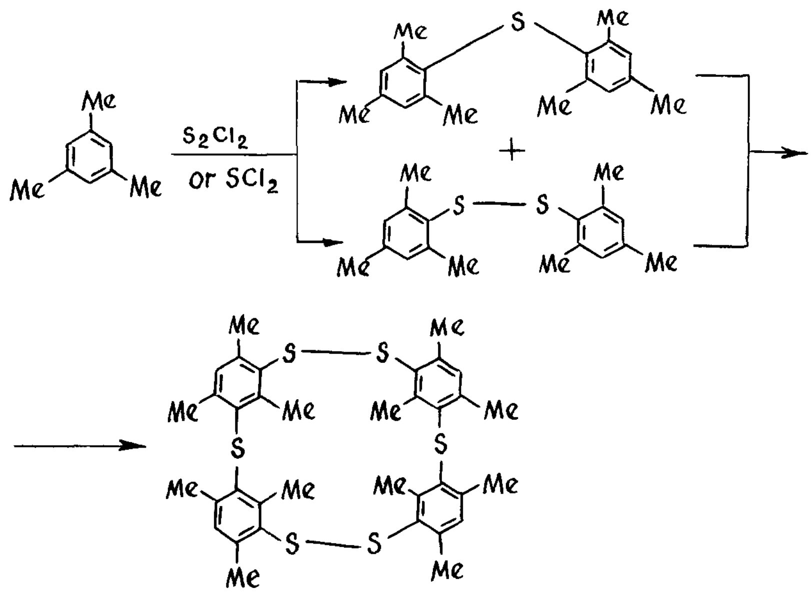


n = 6–8, 10

175a–175d

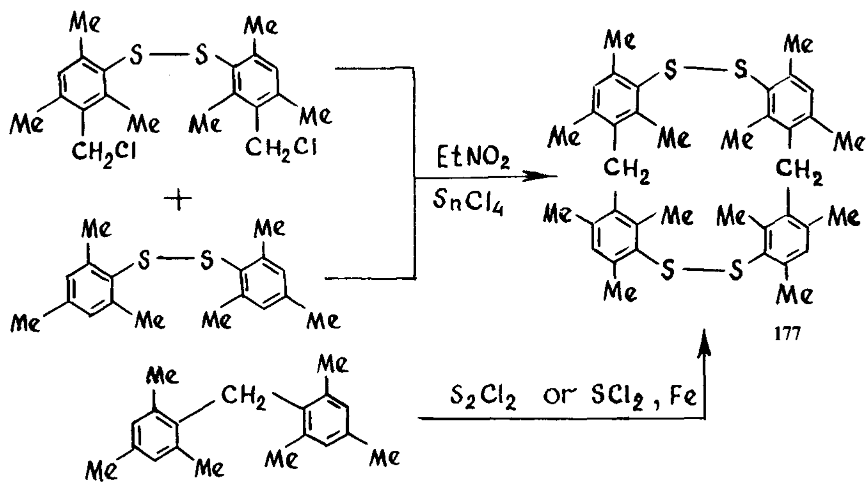
The yields of the above compounds increase with increasing chain length of the α,ω-alkylene-bis(sulfenyl)dithiocarbonates. Thus, with n = 6, 7, 8, and 10 the yields of the corresponding macrocycles are 16, 22, 50, and 86%, respectively.

For the synthesis of the tetranuclear hexathiacyclophane *176* containing two disulfide and two sulfide groups the sulfuration of mesitylene with disulfur dichloride and sulfur dichloride[279] in refluxing chloroform in the presence of iron powder was employed. In the case of S_2Cl_2 the yield of *176* reaches 18% whereas with SCl_2 it does not exceed 3%.



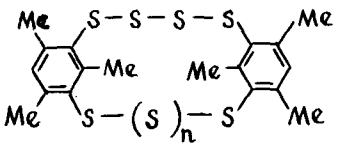
176

The reaction of dimesitylmethane with disulfur dichloride or sulfur dichloride under analogous conditions leads to tetrathia[2.1.2.1]metacyclophane *177* with alternating disulfide and methylene bridges (the yields are 15 and 3%, respectively.)[280]



177

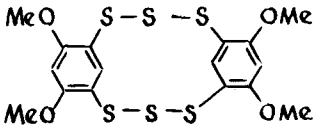
The formation of the unsymmetric hexa- and heptathiacyclophanes *178a* and *178b* in the reaction of mesitylene-2,4-dithiol with sulfur chlorides was quite unexpected.[281]



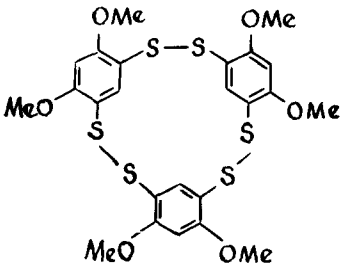
n = 0, 1

178a, 178b

The reaction of 1,3-dimethoxybenzene with disulfur dichloride in the presence of iron powder has been studied both with low and high dilution of the reaction mixture.[282–284] In the first case, linear polysulfides have been prepared. High dilution, however, leads to a mixture of the two macroheterocycles *179a* and *179b* in 6 and 1.5% yield, respectively.

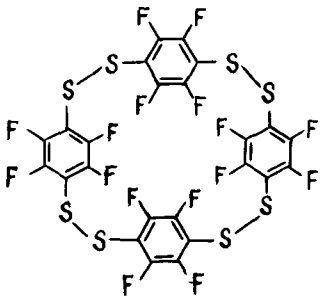


179a



179b

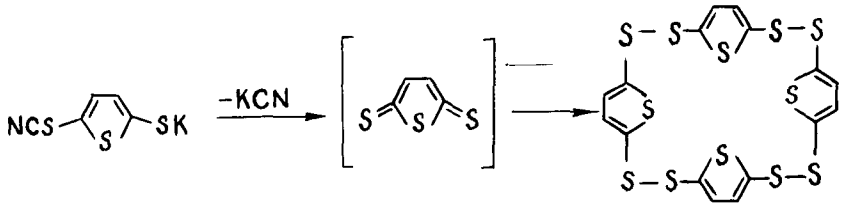
One of the synthetic routes to macroheterocyclic polysulfides is the oxidation of dithiols. Previously it has been reported that the oxidation of 1,4-benzenedithiols gives polymeric disulfides.[285–287] However, treatment of the above compounds with iodine in high dilution gives the macroheterocyclic compound in 30% yield.[288] The oxidation of 1,4-naphthalenedithiol with alkali ferricyanide also affords the macrocyclic compound.[289] The oxidation of tetrafluoro-1,4-benzenedithiol in dimethyl sulfoxide leads to a tetranuclear octathiacyclophane containing four disulfide groups (*180*)



180

in 95% yield.[290] The ready formation of the macroheterocyclic system from tetrafluoro-1,4-benzenedithiol seems quite unique. In contrast, attempts to oxidize 1,4-benzenedithiol, 2,5-dimethoxy-, and tetramethyl-1,4-benzenedithiol under analogous conditions gave only polymers. It was not possible to determine the molecular weight of the tetrachloro-1,4-benzenedithiol oxidation product due to its low volatility and poor solubility.

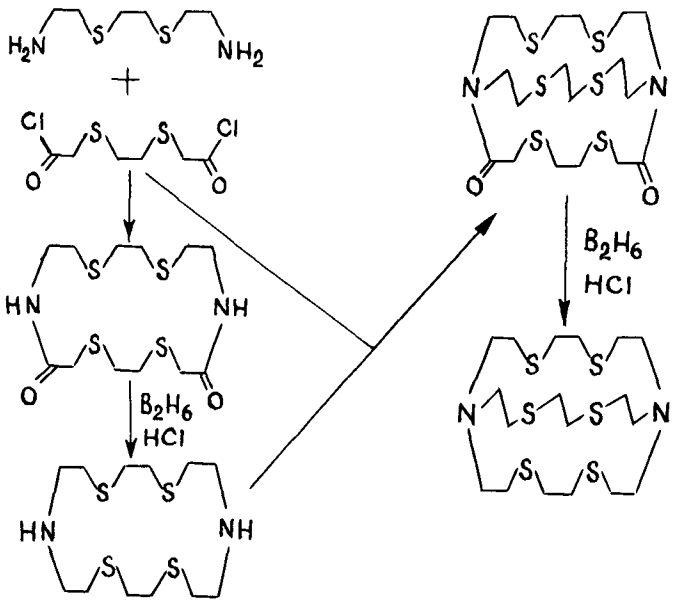
The thiophene analog *181* of the octathiacyclophane *180* has been obtained by treatment of sodium 5-thiocyanato-2-thiophenethiolate with acetic acid and was isolated from a mixture of oligomers in low yield.[227]



181

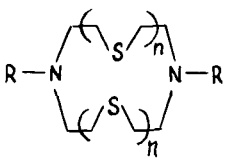
4. Bi- and Tricyclic Systems

In 1969 a series of dimacrocyclic polyamino ethers called cryptands was synthesized.[291,292] A specific feature of these compounds is the remarkable stability of their complexes with cations of numerous metals (Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, etc.). Cryptates are the complexes of bimacrocyclic polyamino ethers, well soluble in water and organic solvents and more stable than

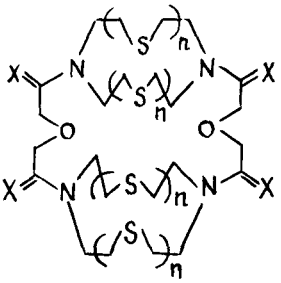


complexes of the corresponding monomacrocycles. Sulfur-containing cryptands were obtained by condensation of oxa- or thiaalkanedicarboxylic dichlorides with 3,6-dithia-1,8-diaminooctane in high dilution.[293] The diamides thus obtained were reduced with diborane and after hydrolysis with hydrochloric acid formed monocyclic diamines. The latter were condensed further with the above dichlorides. The bicyclic diamides formed were reduced with diborane and converted further to the bimacrocycles *182a–187b* in the same way (Table 2).

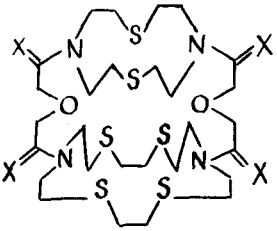
These polymacrocyclic systems can form polynuclear cryptates containing two and more metal cations in the inner cavity of the molecule. At present these systems are of special interest as models of polynuclear biological complexes or homogeneous polynuclear catalysts. A general method for constructing cylindrical trimacrocyclic systems containing different ring sizes and heteroatoms has been suggested. The complexation of the above systems with cuprous and cupric salts has been studied.[294,295] The synthesis of the sulfur-containing trimacrocyclic tetramide *189a* is based on the condensation of the macroheterocycle *188d* possessing reactive substituents at the nitrogen atoms with the macroheterocycle *188a*. Further reduction of the tetraamide *189a* with diborane leads to the cylindrical trimacrocyclic tetrathiatetramine *189b*. The sulfur-containing trimacrocyclic compounds *189c–190b* were obtained in a similar manner.



188a n = 1, R = H
188b n = 1, R = Me
188c n = 1, R = $COCH_2OCH_2COOH$
188d n = 1, R = $COCH_2OCH_2COO$-*p*-$C_6H_4NO_2$
188e n = 2, R = Me
188f n = 2, R = $COCH_2OCH_2COOH$
188g n = 2, R = $COCH_2OCH_2COO$-*p*-$C_6H_4NO_2$



189a n = 1, X = O
189b n = 1, X = H_2
189c n = 2, X = O
189d n = 2, X = H_2

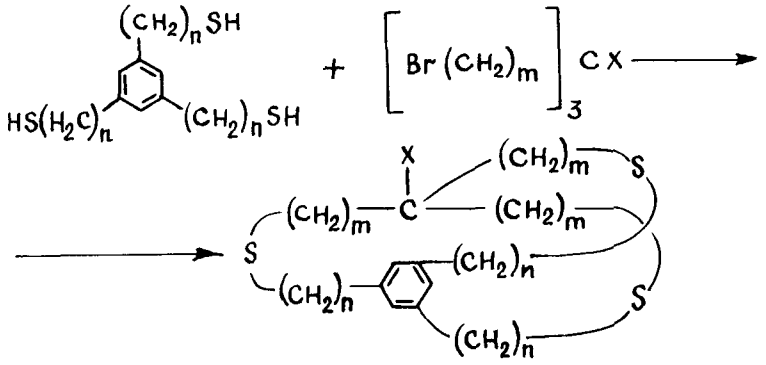


190a X = O
190b X = H_2

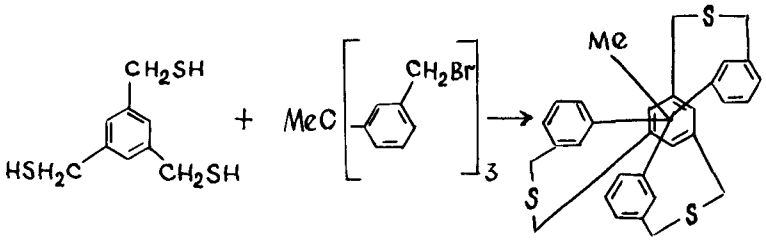
A one-step synthetic route to sulfur-containing bimacrocycles has been developed.[296] The compounds of this type (*191a–191e*) were prepared by reaction of 1,3,5-tris(mercaptomethyl)- or 1,3,5-tris(2-mercaptoethyl)benzene with tris-(bromoalkyl)methanes in the presence of sodium hydroxide.

The reaction of 1,3,5-tris(mercaptomethyl)benzene with methyl-[tris(4-(bromomethyl)phenyl)]methane was also used for the synthesis of the tribridged [2.2.2]cyclophane *192*.[297]

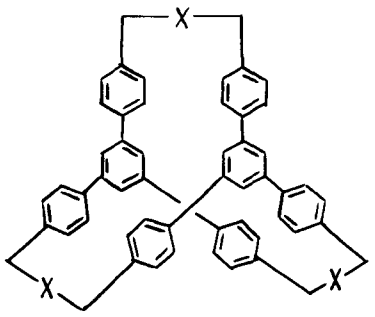
Synthetic routes to the polythiacyclophanes *193a–196* have been reported.[298] The reaction of 1,3,5-tris[(4-mercaptomethyl)-phenyl]benzene with 1,3,5-tris[4-(bromomethyl)phenyl]benzene affords the trithiatriphenylbenzene phane *193a* in 31% yield.



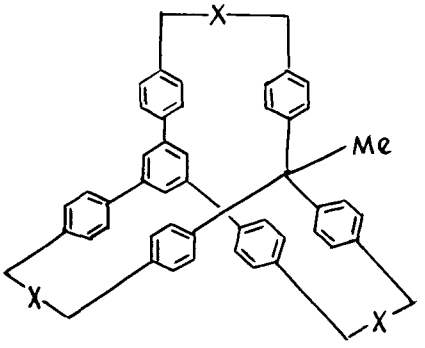
191a n = 1, m = 3, X = H
191b n = 1, m = 2, X = H
191c n = 2, m = 3, X = H
191d n = 2, m = 2, X = H
191e n = 2, m = 1, X = Me



192

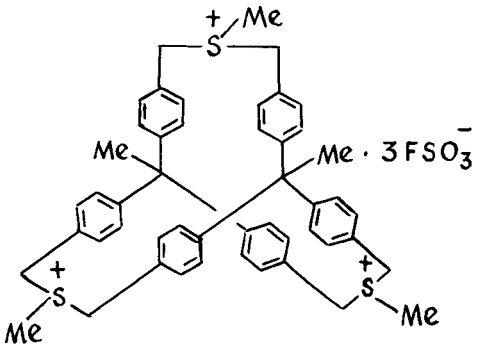


193a X = S
193b X = SO_2
193c X = $^{+}SMeFSO_3^{-}$

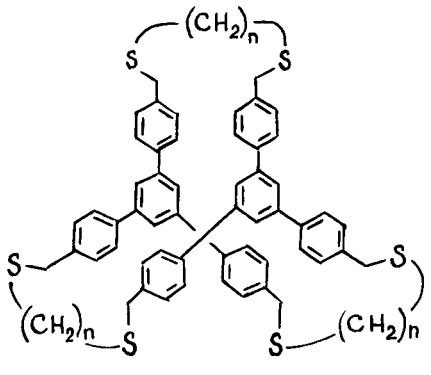


194a X = SO_2
194b X = $^{+}SMeFSO_3^{-}$

The compound *196* was synthesized by reaction of 1,3,5-tris-[4-(bromomethyl)phenyl]benzene with alkane-α,ω-dithiols.



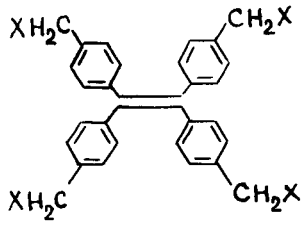
195



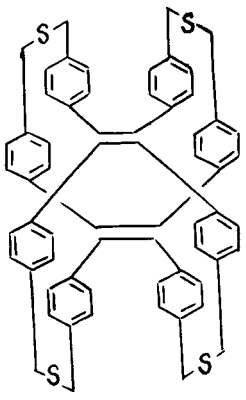
196

n = 2–5

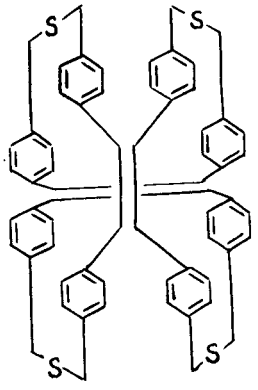
The reaction of equivalent amounts of tetrabromide *197a* and tetrathiol *197b* in high dilution gives a compound with a tetralaterally bridged tetraphenylene system, which is a mixture of two stereoisomers with parallel and orthogonal orientation of the central double bond (compounds *198* and *199*). [299]



197a X = Br
197b X = SH



198



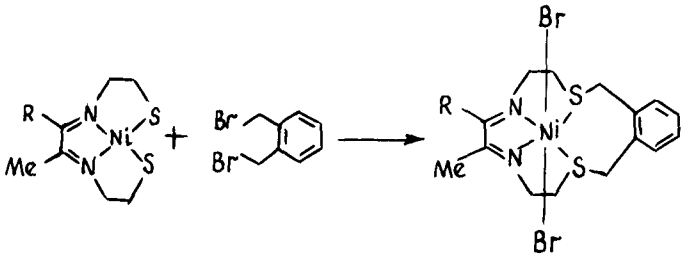
199

5. *Template Synthesis of Sulfur-Containing Macroheterocycles*

In the following a method for preparing sulfur-containing macroheterocycles called "template synthesis" or "matrix synthesis" is discussed. This method is based on

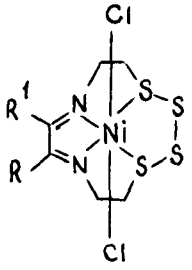
stereochemical arrangement and orientation of reagents by a metal ion or a metal-containing molecule. This allows interaction between the functional groups which under normal conditions is either hindered or impossible.[32]

One of the examples of "template synthesis" is the reaction of α-diketones with mercapto amines in the presence of nickel salts, leading to the tetradentate products *200* which, in turn, when treated with α,α'-dibromo-*o*-xylene, can serve as matrixes for the formation of macrocyclic rings *201*.[300,301]



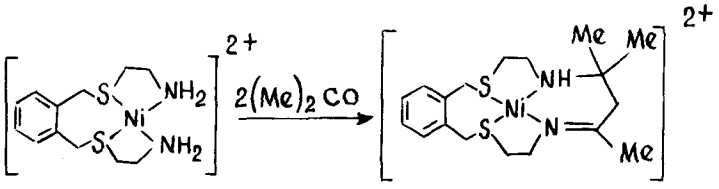
200 201

A similar reaction with disulfur dichloride yields the nickel-containing tetrathiamacrocycloalkane *202*.[302]



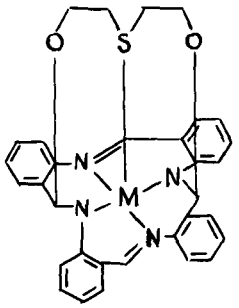
202

The nickel chelate *203* is condensed with acetone according to the foliowing Scheme:[303]



203

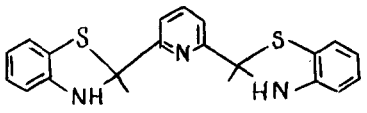
The template reaction of the above $Ni(TAAB)^{2+}$ and $Cu(TAAB)^{2+}$ complexes with bis(2-hydroxyethyl) sulfide leads to coordinated metal compounds with pentadentate "basket-like" macrocyclic ligands.[304–311]



204

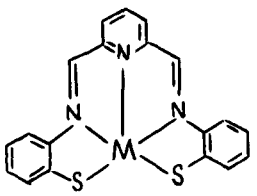
M = Cu, Ni

The product of the reaction of 2,6-diacetylpyridine with 2-aminobenzenethiol *205*,



205

when treated with zinc and cadmium acetate, undergoes intramolecular rearrangement to form the complexes *206* containing a pentadentate ligand.[312,313]

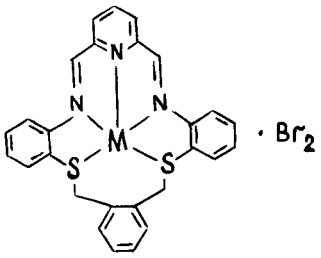


206

M = Zn, Cd

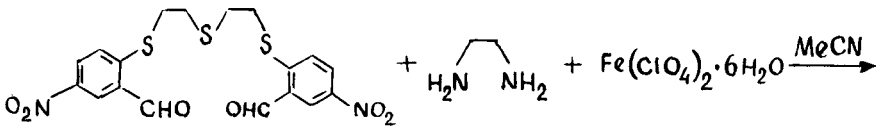
Further template reaction of these compounds with *o*-xylylene dibromide in acetone affords the metal-containing macrocycles *207*.

The reaction of ethylenediamine with a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ and the dialdehyde *208* in acetonitrile leads to the formation of the complex *209*.[314]

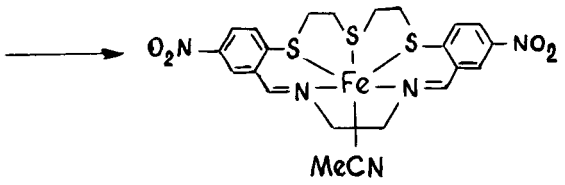


207

M = Zn, Cd

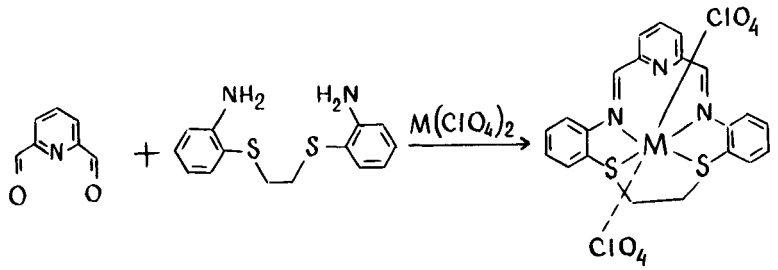


208



209

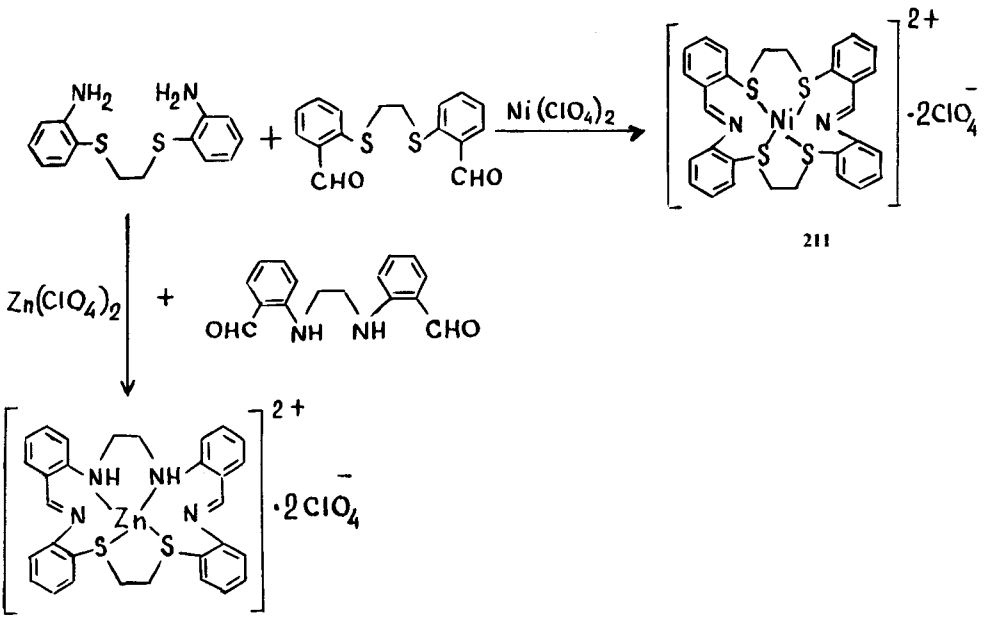
The coordinated compound *210* with a pentadentate sulfur-containing macrocyclic ligand was synthesized according to the Scheme:[315]



210

M = Mn, Zn

The hexadentate macrocyclic complexes *211* and *212* have been prepared by reaction of 1,2-bis(2-aminophenylthio)ethane with 1,4-bis-(2-formylphenyl)-1,4-dithiabutane or 1,4-bis(2-formylphenyl)-1,4-diazabutane, respectively, in the presence of nickel or zinc perchlorate.[316,317]

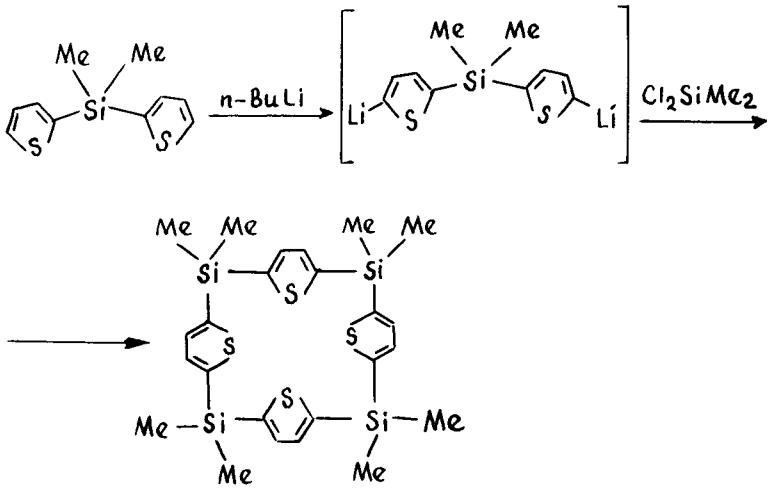


211

212

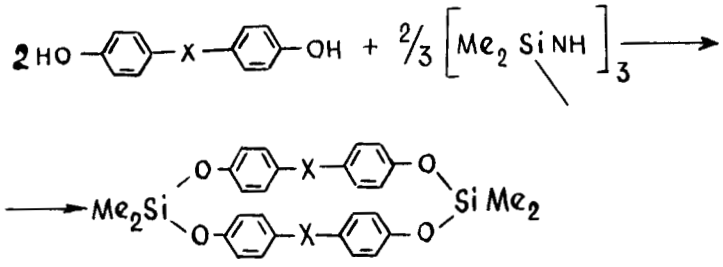
6. Sulfur-Containing Macroheterocycles with Heteroatoms of Inorganogenous Elements

The silathiophenophane *213* has been prepared by reaction of 2,2-bis-(5-lithio-2-thienyl)-2-silapropane with dimethyldichlorosilane in tetrahydrofuran at 0 °C.[319]



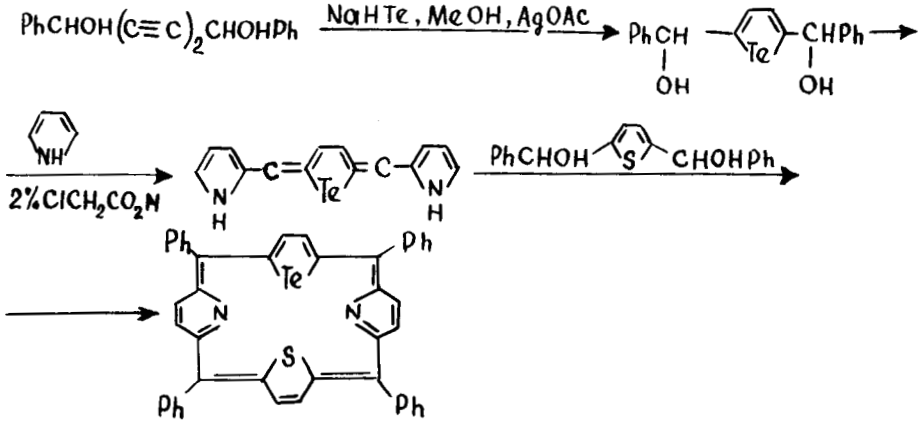
213

Bis(4-hydroxyphenyl) sulfide and bis(4-hydroxyphenyl) sulfone, when treated with hexamethylcyclotrisilazane, form the dithiasilaparacyclophanes *214a* and *214b*, respectively.[320]



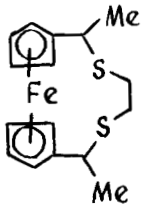
214a X = S
214b X = SO_2

The tetraphenylporphyrin *215*, containing endocyclic sulfur and tellurium atoms, has been synthesized according to the Scheme:[318]

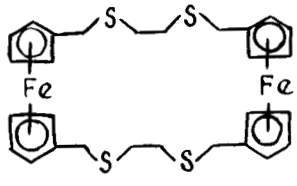


215

The reaction of 1,1-bis(hydroxymethyl)ferrocene and 1,1-bis(1-hydroxyethyl) ferrocene with 1,2-ethanedithol leads to the thiaferrocenophanes *216* and *217* in 34 and 39% yield, respectively.[321–323]



216



217

III. STRUCTURES AND SPECTROSCOPIC CHARACTERISTICS OF SULFUR-CONTAINING MACROHETEROCYCLES AND COMPLEXES THEREOF

I. Oligothiamacrocycloalkanes

1.1. X-Ray diffraction data

According to X-ray diffraction the Ni(*4b*)$^{2+}$ ion structure possesses precisely a square-planar geometry of D_{4h} symmetry, though the ligand ring itself is strongly pleated and twisted.[324] Since the nickel atom is located in the center of the macrocycle the four Ni←S bonds should be coplanar according to crystallographic requirements. The lengths of two of these bonds are equal, the S—Ni—S angle being 90° (Fig. 1, Table 3).

The intraatomic distances and angles in the Cu(*4b*)$(ClO_4)_2$ complex are shown in Table 4. The sulfur atoms in the tetradentate macrocycle occupy four equatorially coordinated sites surrounding the Cu(II) ion.[325] Two perchlorate anions are axially coordinated with the Cu(II) ion at a distance of 2.652(4) Å. The molecule is of symmetry 1 (C_i), i.e., the Cu(II) ion and four sulfur atoms are coplanar. The Cu(*4b*)$(ClO_4)_2$ structure is that of a typical tetragonal Cu(II) complex. As seen from Table 4, the Cu—S bond lengths are equal, 2.297(1) and 2.308(1) Å, while the S—Cu—S bond angles are 90.1(4) and 89.9(4)°. This means that the coordination sphere's equatorial plane is not distorted and corresponds to D_{4h} symmetry.

In the binuclear $(HgCl_2)_2$*4b* complex, all four sulfur atoms in the macrocycle *4b* are exocyclically coordinated to two mercury ions to form two five-membered chelate rings (Fig. 2). The S(1)—Hg—S(2) angle is 83° and the S(2)—Hg bond is longer than the S(1)—Hg bond.[326,327] Each mercury atom is bonded to two sulfurs and two chlorines in an approximately tetrahedral configuration. The tetrahedral configuration of the metal ion is slightly distorted by the arrangement of the chlorine atoms. This geometry is relatively common for Hg(II) complexes, although the exo-conformation of the sulfur atoms in the ligand is quite unique. The preferential formation of five-membered chelate rings as opposed to the more flexible six-membered rings presents one of the most interesting features of this complex conformation (Fig. 2).

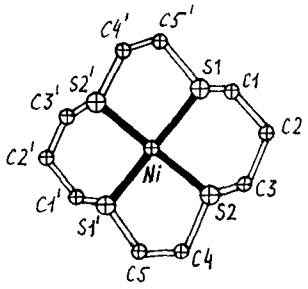


FIGURE 1 Molecular structure of the [Ni(*4b*)]$^{2+}$ cation.

TABLE 3

Intraatomic Distances and Angles in Ni(*4b*)$(BF_4)_2$

Bonds	r, Å	Angles	w, degr.	Angles	w,degr.
Ni—S1	2.177(1)	S1—Ni—S2	90.25(10)	F1—B—F2	111.5(4)
Ni—S2	2.175(1)	Ni—S1—C1	106.9(2)	F1—B—F3	107.9(3)
S1—C1	1.804(6)	Ni—S1—C5′	103.2(2)	F1—B—F4	111.0(5)
S1—C5′	1.821(6)	Ni—S2—C3	107.9(2)	F2—B—F3	108.8(5)
S2—C2	1.800(5)	Ni—S2—C4	103.1(2)	F2—B—F4	107.6(3)
S2—C4	1.808(5)	C1—S1—C5	102.8(3)	F3—B—F4	110.1(3)
C1—C2	1.520(8)	C3—S2—C4	102.6(2)		
C2—C3	1.519(8)	S1—C1—C2	110.6(4)		
C4—C5	1.489(8)	C1—C2—C3	115.0(4)		
B—F1	1.353(7)	C2—C3—S2	111.5(3)		
B—F2	1.343(7)	S2—C4—C5	106.8(2)		
B—F3	1.378(7)	C4—C5—S1′	106.2(2)		
B—F4	1.357(7)				

TABLE 4

Intraatomic Distances and Angles in Cu(*4b*)$(ClO_4)_2$

Bonds	r, Å	Angles	w, degr.	Angles	w, degr.
Cu—S1	2.308(1)	S1′—Cu—S2	89.9(4)	O1—Cl—O2	109.8(3)
Cu—S2	2.297(1)	S1—Cu—S2	90.1(4)	O1—Cl—O3	108.2(2)
Cu—O1	2.652(4)	S1—Cu—O1	97.7(2)	O1—Cl—O4	109.1(3)
S1—C2	1.831(5)	S2—Cu—O1	87.0(2)	O2—Cl—O3	109.5(3)
S1—C3	1.828(5)	Cu—S1′—Cl	100.8(2)	O2—Cl—O4	110.9(3)
S2—C5	1.829(5)	Cu—S2—C2	99.1(2)	O3—Cl—O4	109.3(2)
S2—Cl′	1.825(5)	Cu—S1—C3	104.2(2)		
C1—C2	1.528(5)	Cu—S2—C3	104.7(2)		
C3—C4	1.551(6)	Cu—O1—C1	130.3(2)		
C4—C5	1.550(6)	S1′—C1—C2	107.9(3)		
Cl—O1	1.441(4)	S2—C2—C1	107.7(3)		
Cl—O2	1.421(4)	S2—C5—C4	112.0(4)		
Cl—O3	1.443(4)	S1—C3—C4	109.3(4)		
Cl—O4	1.428(4)	C3—C4—C5	114.9(5)		

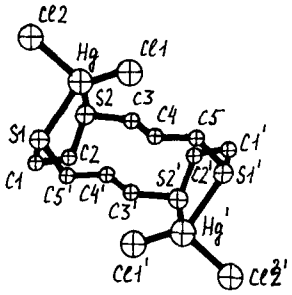


FIGURE 2 Molecular structure of the complex $(HgCl_2)_2$*4b*.

Thus, the X-ray diffraction evidence for Ni(II) and Cu(III) complexes with the sulfur-containing macrocycle *4b* shows that the ligand can exist in the *endo*-conformation whereas in the $(HgCl_2)_2$*4b* complex it is possible for it to assume the *exo*-conformation. The latter seems to be due to the fact that the greater size of two $HgCl_2$ molecules impedes their occupation of the cavity of the macrocycle and makes the complex adopt an extended conformation.

In the molecule $[Hg(4b)(OH)_2][ClO_4]_2$ four sulfur atoms occupy the apexes of the tetragonal-pyramidal base and deviate from this pyramid by no more than +0.15 Å. The Hg—O vector is nearly perpendicular to this plane (82°), while the mercury atom is 0.48 Å above the plane (Fig. 4).[327]

In the Hg(II) complex with the sixteen-membered macrocycle *4c* the four sulfur atoms surround the mercury ion and occupy the apexes of a square at a distance of 2.62 Å from the metal ion. They are alternatively distorted by 0.42 Å from the median plane. The Hg(II) ion is located nearly in the center of the square plane, being displaced from this plane by as little as 0.04 Å. Four *cis*-S—Hg—S angles range within 91.2–91.7° and two *trans*-S—Hg—S angles are 159.6 and 163.5°. The inner coordination sphere is supplemented with two perchlorate anions non-equivalently bound to the mercury cation. One of these anions is monodentante and coordinated to the metal anion at a distance of 2.76 Å, the other in bidentate coordination at a distance of 3.08 and 3.26 Å. Thus, the Hg(II) ion turns to be heptacoordinated, although, in general, the complex presents itself as a distorted elongated octahedron (Fig. 4).[63]

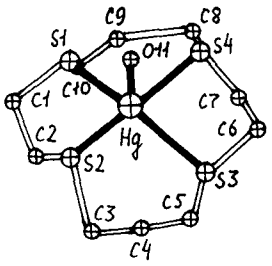


FIGURE 3 Molecular structure of the $[Hg(4b)(OH_2)]^{2+}$ cation.

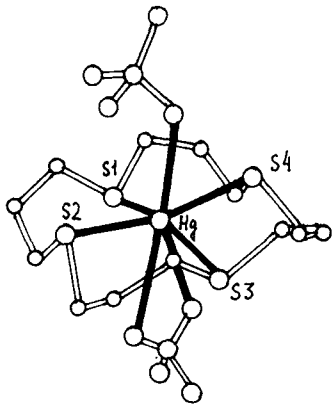


FIGURE 4 Molecular structure of the complex $[Hg(4c)](ClO_4)_2$.

1.2. ^1H NMR spectra

The ^1H NMR spectra of *8b* and TTT (2,5,9,12-tetrathiatridecane) are analogous to that of *4b*. Overlapping singlet-triplet peaks at δ 2.75 p.p.m. correspond to the methylene groups attached to sulfur atoms whereas the multiplet at 2.00 p.p.m. is assigned to the methylene protons not attached to sulfur atoms.[55] The TTT spectrum contains one more singlet at δ 2.16 p.p.m., assigned to methyl protons, whereas the spectrum of *8b* shows two singlets at δ 7.05 and 3.60 p.p.m., assigned to aromatic and benzylic protons, respectively. The ^1H NMR spectrum of $Ni(4b)(BF_4)_2$ is analogous to that of Ni(cyclame)$(ClO_4)_2$, (cyclame is 1,4,8,11-tetraazacyclotetradecane) (Fig. 5).

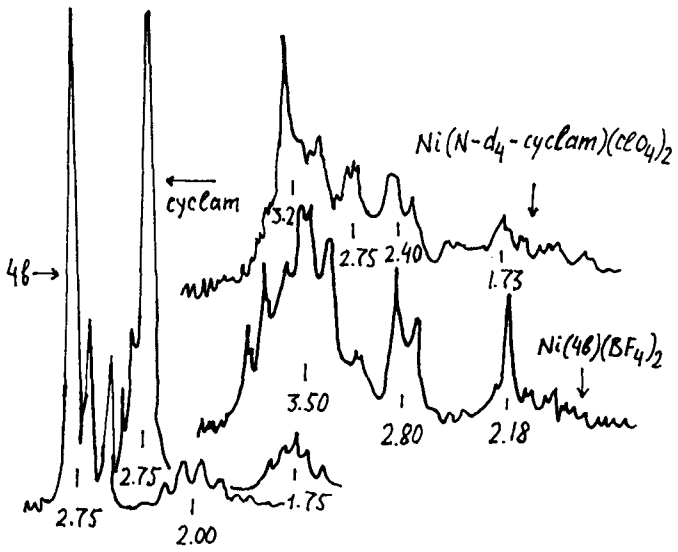


FIGURE 5 NMR spectra of *4b* and its nickel(II) tetrafluoroborate complex as compared to cyclame and its complex.

The great similarity in the spectra of these complexes indicates that the configuration of *4b* with respect to the metal is like that in the Ni complex of cyclame. The spectrum of $Ni(TTT)(BF_4)_2$ is similar in the methylene region, except that the complex TTT displays a singlet at δ 2.50 for methyl groups. The spectrum of the complex *8b*, however, contains a broad singlet at δ 7.51 p.p.m., corresponding to the aromatic protons.

1.3. Infrared spectra

Stretching vibrations of C—S bonds are observed in the IR spectra of macrocyclic sulfides in the 600–700 cm^{-1} region. The C—S bands for the macrocycle *4b* are strongly split and occur in the 675–689 cm^{-1} region. These bands disappear upon complexing.[57] The absorption in the 600–250 cm^{-1} region makes it possible to distinguish *cis*- and *trans*-isomers of complexes of the general formula MA_4Cl_2. The spectrum of the *cis*-octahedral species displays two vibration frequencies due to the metal-chlorine bond, whereas only one vibration frequency is observed when the *trans*-structure is present.

The IR spectra of *cis*-$[Co(4b)Br_2]BF_4$ and *cis*-$[Co(4b)Cl_2]BF_4$ have been studied. The spectrum of the chloro derivative contains two bands at 260 and 336 cm^{-1}, which are not present in that of the bromo derivative. The band position is comparable with that of two bonds of the Co—Cl bond in the *cis*-$[Co(en)_2Cl_2]Cl$ (en = ethylenediamine) complex (210 and 320 cm^{-1}) and this indicates that $[Co(4b)Cl_2]^+$ has the *cis* structure. The spectra of both *4b* and ethylenediamine complexes contain absorption bands occurring between the above-mentioned frequencies, which are likely to be due to Co—S and Co—N stretching, respectively.

The spectra of *trans*-$[Co(8b)Cl_2]ClO_4$ and *trans*-$[Co(8b)Br_2]ClO_4$ have been studied. The spectrum of the chloro complex displays a strong absorption at 383 cm^{-1} which is absent in the spectrum of the bromo derivative. This corresponds to the absorptions at 360 and 384 cm^{-1} of *trans*-$[Co(en)_2Cl_2]Cl$ and *trans*-$[Co(diarsine)_2Cl_2]Cl$, respectively.

Absorption bands at 1698, 1669, 1425, 1264, 787, and 543 cm^{-1} are observed in the IR spectra of the $[Co(8b)(ox)]ClO_4$ complex containing a coordinated oxalate ion.

The infrared spectra of Rh(III) complexes with oligothiacycloalkanes are similar to those of Co(III) complexes.[57] The complexes $[Rh(4b)Cl_2]Cl$, $[Rh(4b)Cl_2]BF_4$, and $[Rh(8b)Cl_2]Cl$ absorb intensively at 304, 288; 308, 288; 290, 280 cm^{-1}, respectively. The presence of two absorption bands is due to the $RhCl_2$ group and associated with frequencies of the complexes with *cis*-configuration described above. There is a close similarity between the frequencies of the *cis*- and *trans*-isomers of the Co and Rh complexes (*trans*: Co 383, Rh 362 cm^{-1}; *cis*: Co 336 and 260 cm^{-1}; Rh 300 and 288 cm^{-1}).

The polymeric (or dimeric) Rh complex with *4b*, $[Rh(4b)Cl]_xCl_{2x}$, absorbs strongly at 326 cm^{-1} with a weak band appearing on the low-energy side at 288 cm^{-1}.

1.4. Electronic spectra

The absorption bands of nickel complexes with *4a*, *8a*, TTD (1,5,9-trithiacyclododecane), and DTH (2,5-dithiahexane) contain three major d-d transitions, ν_1, ν_2, ν_3 (Table 5).[54] These transitions are assigned as follows: $^3A_{2g} \rightarrow {}^3T_{2g}$

(ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3). There is a shoulder on the low-energy side of the ν_1 transition. The origin of this shoulder is not clear, but one can speculate that it may be a transition from the ground state to the lowest-lying singlet state, i.e., ^1E_g (D). This may be due to a ligand distorsion about the metal from the regular octahedral configuration. The D_q values calculated for these complexes from the electronic spectra are within 1040–1120 cm^{-1}. The Racah parameters B have been calculated as well and are given in Table 5. The B values allow the complexes to be classified into two groups. Those possessing two nickel atoms in the molecule have values in the neighborhood of 900 cm^{-1}, while the complexes with only one nickel atom in the molecule have values of about 725 cm^{-1}. These two groups differ also in the molar extinction coefficients of their absorption bands, being are higher for the former than the latter.

The electronic spectra of Ni complexes of the general formula Ni(*4b*)X_2 where X = BF_4, ClO_4, Cl, Br, I, or NCS, as well as those of Ni(*8b*)$(BF_4)_2$ and Ni(TTX)$(BF_4)_2$ are shown in Table 6.[55] The spectra of the low-spin Ni(*4b*)$(ClO_4)_2$ and Ni(*4b*)$(BF_4)_2$ complexes with an intense singlet near 500 nm and a molar extinction coefficient of about 270 give evidence for a square-planar structure of these complexes. The spectra of the high-spin Ni(*4b*)X_2 complexes (X = Cl, Br, I, NCS) contain four different bands in the near infra-red and visible regions (Table 6). The spectra of solutions of these complexes in nitromethane are identical with those of the solid complexes except in the case of the I^- ion-containing complex. From the spectra

TABLE 5.

Electronic Spectra of Nickel Complexes of the Type $Ni_nL_m(BF_4)_p$

				λ_{max}, nm		
L	**n**	**m**	**p**	**CH_3NO_2**	**solid**	**B, cm^{-1}**
8a	2	3	4	1000 sh (120)	1000 sh	
				877 (156) ν_1	892 ν_1	907
				526 (238) ν_2	526 ν_2	
4a	2	3	4	1052 sh (139)	1075	
				952 (181) ν_1	961 ν_1	880
				581 (67) ν_2	575 ν_2	
					370 ν_3	
TTD	1	2	2	970 sh (12)	980 sh	
				892 (18) ν_1	900 ν_1	713
				571 (31) ν_2	565 ν_2	
					380 ν_3	
DTH	1	3	2	1000 sh (22)	1031 sh	747
				900 (37) ν_1	917 ν_1	
				575 (33) ν_2	581 ν_2	
					375 ν_3	

TABLE 6

Electronic Spectra of Nickel Complexes of the Type $Ni(L)X_2$

		λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)				λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	
L	X	CH_3NO_2	solid	L	X	CH_3NO_2	solid
TTX	BF_4	495 (268)		*4b*	Br	1110 (16) sh	1120
8b	BF_4	510 (273)	515			939 (48)	910
		450 (142) sh	455 sh			610 (53)	590
4b	BF_4	494 (263)	496	*4b*	Cl	1080 (25) sh	1090 sh
		416 (97.5) sh	414			940 (48)	900
4b	ClO_4	492 (270)	496			610 (28)	590
		420 (100) sh	410				340
4b	I	700 (58) sh	1210	*4b*	NCS	1010 (34) sh	1010
		540 (315)	910			915 (54)	901
						570 (28)	570
							350

of these tetragonal complexes the Dq^{2y} value was calculated. The Dq^{2y} value for the ligand *4b* (1070 cm^{-1}) is weak, but nevertheless visible.

For an octahedral complex of cobalt(III) two bands with a maximum molar extinction coefficient of about 100[57] were ascribed to the spin-allowed transitions $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$ in the visible and near ultraviolet region, respectively. In the spectra of complexes of the type *trans*-$[CoA_4X_2]^{n+}$ with D_{4h} symmetry, the lower-energy band splits into two components. For the *cis*-isomers, the first band splitting is so small that only one band is observed.

The $[Co(4b)X_2]^+$ complexes with X = Cl, Br, NCS, and $\frac{1}{2}C_2O_4$ display absorption bands at 540 nm (Table 7).[57] The second band is observed near the 416 nm region as a shoulder of a strong absorption centered at approximately 385–357 nm. The band maxima and extinction coefficients for the first transition are given in Table 8. For comparison, the data for the *cis*-tetramine complexes of cobalt(III) in this Table are also given. The positions of the band maxima for these tetrakissulfide complexes are close to those found for *cis*-tetramine complexes and differ greatly from the spectra of the *trans*-tetramine complexes of cobalt(III) (Table 9). This confirms the assignment of a *cis*-structure of these complexes. A *cis*-configuration must be assumed for the $[Co(4b)(ox)]ClO_4$ complex because of the bidentate nature of the oxalate ligand.

The spectral difference between *cis*- and *trans*-dinitro complexes of Co(III) is less clear-cut; however, the dinitro complexes prepared by substitution on *cis*-$[Co(4b)Cl_2]^+$ all gave identical visible absorption spectra and are all assumed to be *cis*.

The $Co(4b)I_2B(C_6H_5)_4$ complex exhibits its first absorption maximum at 641 nm. The position of this band is close to those found in the spectra of *trans*-tetramine complexes of cobalt(III) (Table 9). The second component of this band splitting appears at 470 nm. Using the crystalline field model, the following spectral parameters have been calculated: Dq^{xy} = 2420 cm^{-1}, Dt = 545 cm^{-1}, Dq^z = 1465 cm^{-1}.

TABLE 7

Electronic Spectra of Complexes of Cobalt(III) with *4b*

Compound	λ_{max}, nm		
	CH_3OH	CH_3NO_2	solid
cis-[Co(*4b*)Cl_2]BF_4	535	533	540
	420	420	429
	340		350
cis-[Co(*4b*)BR_2]BF_4	550	550	550
			461
	310		390
cis-[Co(*4b*)$(NCS)_2$]$B(C_6H_5)_4$	540	540	540
	420	420	440
	298		300
cis-[Co(*4b*)$(NO_2)_2$]BF_4	470	470	480
			390
			335
trans-[Co(*4b*)I_2]$B(C_6H_5)_4$	640	640	640
	490	490	500
	328		

TABLE 8

Electronic Spectra of Complexes of Cobalt(III) with Polyamines and Polysulfides

Compound	Solvent	λ_{max}, nm (ε)[a]	λ_{max}, nm (ε)[a]
cis-[Co$(en)_2Cl_2$]$^+$	H_2O	530 (78)	380 (69)
cis-[Co(trien)Cl_2]$^+$	dil $HClO_4$	539 (130)	381 (135)
cis-[Co(cyclen)Cl_2]$^+$	30% HCl	560 (185)	390 (165)
cis-[Co(cyclam)Cl_2]$^+$		558 (105)	
cis-[Co(*4b*)Cl_2]$^+$	CH_3NO_2	533 (654)	420
cis-[Co$(en)_2Br_2$]$^+$	H_2O	560 (110)	
cis-[Co(cyclen)Br_2]$^+$	HBr	570 (180)	390 (170)
cis-[Co(*4b*)Br_2]$^+$	CH_3NO_2	550 (640)	
[Co$(en)_2(C_2O_4)$]$^+$		500 (113)	355 (144)
[Co(cyclen)(C_2O_4)]$^+$	H_2O	520 (245)	365 (205)
[Co(*4b*)(C_2O_4)]$^+$	CH_3NO_2	528 (579)	
cis-[Co$(en)_2(NO_2)_2$]$^+$	H_2O	435 (182)	
cis-[Co(cyclen)(NO_2)]$^+$	H_2O	445 (355)	320 (4460)
cis-[Co(cyclam)$(NO_2)_2$]$^+$		465 (279)	
cis-[Co(*4b*)$(NO_2)_2$]$^+$	CH_3NO_2	470 (814)	
cis-[Co(cyclam)$(NCS)_2$]$^+$		510 (392)	
cis-[Co(*4b*)(NCS)]$^+$	CH_3NO_2	540 (840)	420

[a] $l \cdot mole^{-1} \cdot cm^{-1}$

TABLE 9

Electronic Spectra of *trans*-Tetramine and *trans*-Tetrathiacycloalkane Complexes of Cobalt(III)

Compound	λ_{max}, nm (ε)[a]	λ_{max}, nm (ε)[a]
trans-$[Co(en)_2Cl_2]^+$	617 (34)	388 (36)
trans-$[Co(cyclame)Cl_2]^+$	637 (31)	431 (41)
trans-$[Co(4b)I_2]^+$	640 (820)	470 (3420)
trans-$[Co(8b)Cl_2]^+$	630 (69)	
trans-$[Co(8b)Br_2]^+$	660 (80)	

[a] $l \cdot mole^{-1} \cdot cm^{-1}$

Comparison of the ligand parameters, Dq^x for *4b* with those for the *trans*-tetramino complexes $[Co(NH_3)_4Cl_2]^+$, $[Co(en)_2Cl_2]^+$, $[Co(en)_2Br_2]^+$, $[Co(1,4\text{-CT})Cl_2]^+$, and $[Co(1,7\text{-CT})Br_2]^+$, 2278, 2530, 2530, 2640, and 2620 cm^{-1}, respectively, shows that the sulfide donor ligand can exert an in-plane ligand strength similar to that of nitrogen donor ligands.

The complexes $[Co(8b)Cl_2]ClO_4$ and $[Co(8b)Br_2]ClO_4$ exhibit spectra similar to that found for *trans*-$[Co(4b)I_2]B(C_6H_5)_4$, with the first component of the split band at 630 and 660 nm, respectively. The second component of this spin-allowed transition is obscured by an intense charge-transfer transition, therefore calculation of ligand field parameters is not warranted.

Comparison of the extinction coefficients in the spectra of the *cis*-complexes (Table 8) shows that those of the sulfide ligand are several times larger than those of the *cis*-tetramines. This presumably reflects an increase in the covalent nature of the metal-ligand bond. Also larger extinction coefficients for the d-d transitions are predicted for *cis*-isomers and this is borne out in the case of the *4b* and *8b* complexes (ε from 500 to 800 $l \cdot mole^{-1} \cdot cm^{-1}$ for *cis*-isomers and ε 69–80 $l \cdot mole^{-1} \cdot cm^{-1}$ for *trans*-isomers).

The spectra of the Rh(III) complexes with the tetrakissulfides *4b* and *8b* exhibit absorption bands analogous to those of Rh(III) *cis*-complexes with tetramines (Table 10).

1.5. Molar conductance

The tetrafluoroborate 2:1 complexes of Ni(II) with oligosulfides are diamagnetic electrolytes (Table 11). The thiocyanate, chloride, and bromide complexes with *4b* are paramagnetic non-electrolytes in nitromethane solution whereas the iodine complex possesses some conduction depending on the solvent concentration.[55] The molar conductance values of the TTD and DTH complexes show the latter to be typical 2:1 electrolytes.[54] These values for the complexes *4a* and *8a* are considerably higher than for TTD and DTH, therefore a "dimer" structure may be assumed for these complexes.

TABLE 10

Electronic Spectra of Tetrathiacycloalkane and Cyclame Complexes of Rhodium(III)

Compound	λ_{max}, nm (ε)[a] (H_2O)
[Rh(*4b*)Cl_2]Cl	350 (2270), 320 sh (1900), 252 (26950)
[Rh(*8b*)Cl_2]Cl	350 (1935), 255 (20300)
[Rh(*4b*)Br_2]Br	370 (2180), 245 (24150)
[Rh(*4b*)I_2]I	405 (2460), 320 (8550), 245 (22550)
cis-[Rh(cyclame)Cl_2]$^+$	354 (233), 299 (308), 207 (33900)
cis-[Rh(cyclame)Br_2]$^+$	367 (243), 309 (871)

[a] $l \cdot mole^{-1} \cdot cm^{-1}$

TABLE 11

Magnetic Moments and Molar Conductance of Nickel(II) Complexes of the Type $Ni_n(L)_mX_p$

Compound	μ(BM)	$\Lambda(M^a)$	Compound	μ(BM)	$\Lambda(M^a)$
Ni_2(*4a*)$_3(BF_4)_4$	3.06	318	Ni(TTD)$_2(BF_4)_2$	3.19	186
Ni_2(*8a*)$_3(BF_4)_4$	3.07	334	Ni(DTH)$_3(BF_4)_2$	3.15	182
Ni(TTT)$(BF_4)_2$	n[b]	186	Ni(*4b*)Br_2	3.18	18.1
Ni(*8b*)$(BF_4)_2$	n	187	Ni(*4b*)Cl_2	3.04	23.9
Ni(*4b*)$(BF_4)_2$	n	194	Ni(*4b*)$(NCS)_2$	3.11	27.7
Ni(*4b*)$(ClO_4)_2$	n	189	Ni(*4b*)I_2	3.10	concentration dependent

[a] $ohm \cdot cm^2 \cdot mole^{-1}$; [b] n stands for low-spin complex

The molar conductance of Co(III)-*4b* and Co(III)-*8b* complexes in nitromethane indicates that they are typical 1:1 electrolytes.[57] The molar conductance of rhodium complexes is slightly lower than that of analogous cobalt (III) complexes. The rhodium complexes, however, seem to be 1:1 electrolytes as well (Table 12). This is consistent with the tetradentate ligand occupying four of the six sites of the octahedral coordination sphere of rhodium(III).

1.6. Magnetic properties

The Ni(TTT)$(BF_4)_2$, Ni(8b)$(BF_4)_2$, Ni(*4b*)$(BF_4)_2$, and Ni(*4b*)$(ClO_4)_2$ complexes are low-spin ones (Table 11). The magnetic moments of other Ni(II) complexes with the oligothiacycloalkanes *4a*, *4b*, *8a*, TTD, and DTH show those to be high-spin complexes (Table 11).[54,55] The magnetic moments of these compounds in both the solid form or in nitromethane solution lie within 3.0–3.2 BM.

TABLE 12

Molar Conductance of Tetrathiacycloalkane Complexes of Cobalt(III) and Rhodium(III)

Compound	Λ(M[a])	Compound	Λ(M[a])
cis-[Co(*4b*)Cl_2]BF_4	95	[Rh(*8b*)Cl_2]Cl	78
cis-[Co(*4b*)Br_2]BF_4	92	[Rh(*4b*)Br_2]Br	78
cis-[Co(*4b*)$(NO_2)_2$]BF_4	98	[Rh(*4b*)I_2]I	76
cis-[Co(*4b*)$(NCS)_2$]$B(C_6H_5)_4$	69	[Rh(*4b*)Cl_2]BF_4	79
trans-[Co(*4b*)I_2]$B(C_6H_5)_4$	54	[Rh(*4b*)$(NO_2)_2$]$B(C_6H_5)_4$	69
[Rh(*4b*)Cl_2]Cl	74	[Rh(*4b*)Cl_2]$B(C_6H_5)_4$	65

[a] ohm·cm^2·mole^{-1}

The spin-spaired Co(III) complexes with *4b* and *8b* exhibit a small paramagnetism of the temperature independent type.[57] This indicates that the Co-containing compounds are in the 3+ oxidation state.

The magnetic moments for the [Rh(*4b*)X_2]$^+$ complexes with X = Cl, Br, I, and NO_2 lie in the range 0–0.69 μ BM and are in agreement with a spin-paired d^6 electronic configuration of the metal ion.[57]

2. *Oligothiacyclophanes and Their Analogs*

2.1. *Crystal and molecular structures of thiophenophanes*

The thiophenophane *156m* displays a regular C_i symmetry and nearly corresponds to C_{2h} symmetry.[328] The thiophene rings resemble an open envelope since the sulfur atom is by 0.196 Å displaced from the plane of the four carbon atoms. The bond lengths in the thiophene rings of thiophene, 2-thiophenecarboxylic acid, and thiophenophane *156m* differ only negligibly (Table 13). The S—C(2) and C(3)—C(4) bond lengths increase in the series: 2-thiophenecarboxylic acid < thiophene < thiophenophane. The heterocycle valence angles in thiophene and 2-thiophenecarboxylic

TABLE 13

Bond Lengths and Angles in Thiophenophane, Thiophene, and 2-Thiophenecarboxylic Acid

Bonds and angles	Thiophenophane *156m*	Thiophene	2-Thiophenecarboxylic acid
S—C(2)	1.728(2)	1.714(1)	1.698(10)
C(2)—C(3)	1.369(2)	1.370(2)	1.362(11)
C(3)—C(4)	1.435(2)	1.423(2)	1.414(11)
S—C(2)—C(3)	109.5(1)	111.5(2)	111.8(5)
C(2)—C(3)—C(4)	113.3(2)	112.4(2)	112.2(7)
C(2)—S—C(5)	93.43(6)	92.2(1)	92.1(4)

acid are nearly equal. In the thiophenophane molecule, however, the angles at the S and C(3) atoms are greater and the angle at the C(2) atom is smaller than the standard value. The lower (by 2°) S—C(2)—C(3) angle value is consistent with an analogous phenomenon observed in [2.2](2,5)bipyridinophane and [2.2]cyclophanes where the angles at prebridge atoms lie considerably below the normal values.

The CH_2—CH_2 bridge geometry in the thiophenophane *156m* is characterized by a strained C—C bond length of 1.592 Å and angles of 112.3(1) and 113.5(1)° (the torsion angle being equal to 34.4°). The bond length between the sulfur atoms in the thiophene rings is 3.225(1) Å. The interatomic distances S . . . C(2′) and S . . . C(5′) are 3.071(1) and 3:109(1) Å, S . . . C(3′) and S . . . C(4′) being 3.174(1) and 3.197(1) Å, respectively. Thus, each sulfur atom in the thiophenophane *156m* lies above the median point of the opposite thiophene ring (Fig. 6).

The conformation of macrocyclic keto lactones containing a thiophene ring such as *158a*, *158c*, *158e*, and *158f* is characterized by four planar fragments, i.e., the thiophene ring, the carbonyl group plane, the lactone group plane, and the planar portion of the polymethylene chain[245,250,251]. The thiophene ring in compounds *158a* and *158c* is planar (Fig. 7,8). However, the external valence bonds C(14)-C(1) and C(11)-C(10) in the macrocycle deviate from the thiophene ring plane by 9.5 and 8.8°

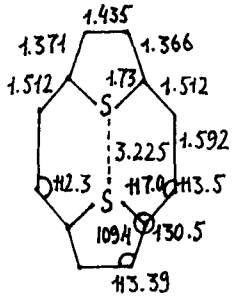


FIGURE 6 Bond lengths Å and angles (°) for thiophenophane *156m*.

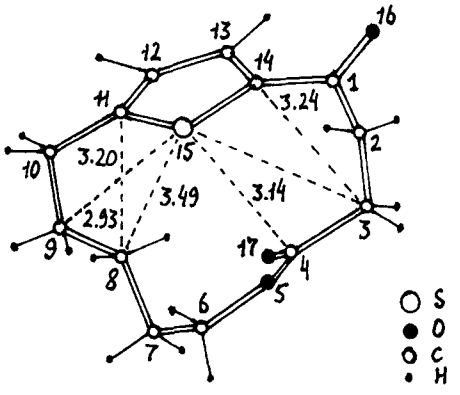


FIGURE 7 Molecular geometry of cyclophane *158a*.

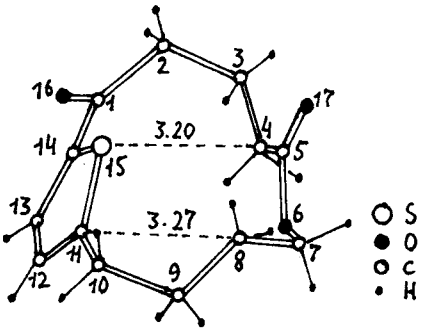


FIGURE 8 Molecular geometry of cyclophane *158c*.

for compound *158a* and by 8.6 and 6.9° for compound *158c*. This leads to displacement of atoms C(1) and C(10) by 0.24 and 0.23 Å, respectively, (*158a*) and 0.22 and 0.18 Å, respectively, (*158c*) towards the *ansa*-bridge.

The thiophene ring in compounds *158e* and *158f* is not absolutely planar. The thiophene ring non-coplanarity is clearly manifested by a 0.04 Å deviation of atoms C(11) and C(14) from the plane S(15)C(12)C(13) towards the *ansa*-bridge.

The carbonyl group planes are twisted by 19.5 (*158a*), 14.5 (*158c*), 15.8 (*158e*), and 18.4° (*158f*) with respect to the thiophene ring. This seems to be caused by intramolecular repulsion of the *ansa*-bridge atoms from the thiophene ring plane. The thenoyl fragment displays an *O,S-trans*-conformation. This is somewhat unexpected for thenoyl fragments. Acylic thiophene derivatives containing the carbonyl group in the α-position possess as a rule an *O,S-cis*-conformation.

The C=O bond length in the thenoyl fragment is slightly larger than that of the lactone C=O bond. The C(1)-C(14) distance (1.45 and 1.46 Å) is markedly shorter than the standard Csp^2-Csp^2 value (1.48 Å). This provides evidence for carbonyl group-thiophene ring conjugation.

The *O,S-cis*-conformation of the thenoyl fragment in *158e* is unexpected. However, according to NMR spectroscopic data including work with magnetic shift reagents (PSR), compounds *158a*, *158c*, *158e*, and *158f* in solution exhibit an *O,S-trans*-conformation. The conformational difference of compound *158e* in the crystalline state and in solution is possibly caused by the solvent effect and complexing with PSR.

The lactone group in macrocyclic keto lactones is planar and displays a *trans*-configuration. The bond lengths and the corresponding valence angles in the lactone group in the isomers *158a*, *158c*, *158e*, and *158f* are nearly equal and independent of both the group position and the ring strain.

As a result of transannular repulsion of the *ansa*-bridge atoms from the thiophene ring the polymethylene chain of the macrocycles *158a* and *158c* is expanded due to a strong deformation of the valence angles C(3), C(7), C(8), and C(9) in *158a* and C(3), C(8), and C(9) in *158c*. The C—C interatomic distances are close to the standard values of the Csp^3-Csp^3 bond. In *158e* the *ansa*-bridge C(3) . . . C(9) displays a zig-zag form, however, some of its units are in closer contact with the thiophene ring π-electronic system than in compounds *158a*, *158c*, and *158f* due to the *O,S-cis*-conformation of the thenoyl fragment in *158e*.

The analysis of intramolecular contacts in compounds *158a*, *158c*, *158e*, and *158f* indicates short transannular distances. In these compounds the following atoms are very close to each other: C(11)...C(8) (2.93 Å), S(15)...C(9) (3.20 Å), S(15)...C(4) (3.14 Å), S(15)...C(8) (3.49 Å), C(14)...C(3) (3.24 Å) for *158a*; C(11)...C(8) (3.27 Å), S(15)...C(5) (3.20 Å), S(15)...C(4) (3.34 Å) for *158c*; C(11)...C(8) (2.98 Å), C(13)...C(6) (3.28 Å), C(11)...O(7) (2.95 Å), C(12) ... C(6) (3.37 Å), C(14) ... C(5) (3.28 Å) for *158e*. The right moiety of the molecule *158f* is not hindered sterically since the intramolecular distances are close to the sums of the van der Waals radii for the corresponding atoms. At the same time, the molecular moiety on the left from the lactone group is considerably hindered due to steric factors, i.e., the transannular distances C(11)...O(8) and S(15)...O(8) (2.94 and 3.12 Å, respectively) are much smaller than the sums of the van der Waals radii.

The intermolecular contacts in the crystal lattice of these compounds are close to the sums of the van der Waals radii of the corresponding atom pairs; no anomalously short intermolecular distances are observed. There are molecules of two mirror-rotation forms in the crystal lattices of *158c* and *158f*.

3. *Macroheterocycles Containing Endocyclic Di- and Polysulfide Groups*

3.1. *X-Ray diffraction*

According to the X-ray pattern compound *174* contains four nearly planar S—C—C—S groups[277]. Two sulfur atoms in the planar S—C—C—S fragment are in the *trans*-position to each other, the CH_2 and $C(CH_3)_2$ groups being criss-cross with respect to the two bonded $CH_2SSC(CH_3)_2$ groups. The carbon atoms of the CH_2 groups deviate from the least-square S—C—C—S plane. The hydrogen atoms, 2.7–2.8 Å apart, are turned inside towards the center of the ring. These values are slightly greater than hydrogen van der Waals radii (2.4 Å), therefore *174* is relatively free from steric hindrance. This macroheterocycle contains bonds of four types: S—S, S—CH_2, S—$C(CH_3)_2$ and CH_2—$C(CH_3)_2$. Thus, the X-ray diffraction study of this compound shows that *174* is a symmetric 16-membered cyclic tetramer of C_i symmetry.

3.2. *^1H and ^{19}F NMR spectra*

The ^1H NMR spectral parameters of hexathia[3.3]metacyclophane *179a* include two signals of intraannular and external phenylene protons in the aromatic regions[283].

The intraannular aryl protons resonate at very low field (δ 8.26-8.40 ppm) as compared with the signals of the corresponding protons in the ^1H NMR spectrum of 2,11-dithia[3.3]metacyclophane (δ 6.63 ppm) and 1,3,10,12-tetrathia[3.3]-metacyclophane (δ 7.2 ppm). These low-field absorptions are indicative of a *syn*-conformation of hexathia[3.3]metacyclophane *179a* (Fig. 9). This is confirmed by X-ray structural data of this compound and by the absence of temperature-variable dependences of ^1H NMR spectral parameters.

The ^1H NMR spectral parameters of the intraannularly methyl substituted polythiametacyclophanes *178a* and *178b* contain signals of methyl groups of three

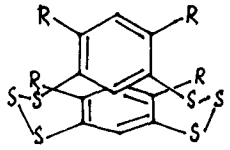


FIGURE 9 *syn*-Conformation of metacyclophane *179a*.

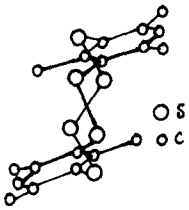


FIGURE 10 *anti*-Conformation of metacyclophane *178a*.

types[281,283]. Taking into account a supplementary deshielding effect of neighboring sulfur atoms, the lower-field signals (δ 2.71 and 2.78 ppm for *178a* and *178b*, respectively) may be attributed to methyl groups attached to the tetrasulfide bridge and the other signals (δ 2.55 for *178a* and 2.63 ppm for *178b*) to the methyl groups bonded to the disulfide or trisulfide bridge, respectively. Despite the deshielding effect of the surrounding sulfur atoms the intraannular groups resonate at higher field (δ 1.78 ppm and 2.08 ppm in *178a* and *178b*, respectively) than the corresponding protons in 2,4-bis(methylthio)mesitylene (δ 2.90 ppm). These protons are likely to be shielded by the opposite aromatic rings. Thus, the *anti*-conformation shown in Fig. 10 is most probable for compound *178a*.

For compound *180* four possible conformations have been suggested: *cis*, *trans*, alternation of *cis* and *trans*, and *cis-cis-trans-trans*. According to ^{19}F NMR evidence, conformational transformations of *180* do occur within the temperature range $-60 - +140$ °C. At 26 °C broadened peaks of equal area in the -128.8 and -132.7 ppm region appear. Besides, a minor peak (15% of the area of any major peak at -129.9 ppm) is observed. The fourth signal occurs as a higher field inflection of the peak at -128.8 ppm. With increasing the temperature to +55 °C and higher, a single peak at -131.2 ppm appears. When the temperature drops again to +26 °C and further to -65 °C all peaks appear. The different width and form of these peaks are indicative of F-F interaction. This interaction is clearly manifested as a limited rotation of phenyl rings at low temperatures. The calculated rotational energy barrier is 18.2 kcal/mole. Thus, it is assumed that the two major peaks are caused by two different sets of fluorines which all can be involved in either *cis*- or *trans*-conformation.

4. Tricyclic Systems

4.1 X-Ray diffraction data

According to the X-ray diffraction data the complex *189b* contains two Cu(II) ions localized inside the molecular cavity of the macrocyclic ligands[295]. Each cation is

attached to two nitrogens, two sulfurs, and one oxygen atom. The molecule possesses a center of symmetry and the shape of a distorted tetragonal pyramid in which the metal ion is displaced by approximately 0.34 Å from the main N_2S_2 plane towards the axial oxygen atom. The lengths of the four Cu—N and the four Cu—S bonds range within 2.020(5)–2.058(5) and 2.306(1)–2.331(1) Å, respectively. The interatomic Cu(1)–O(4) and Cu(2)–O(16) bond lengths are 2.291(5) and 2.283(4) Å, respectively. The Cu(1)...Cu(2) distance is 5.621 (1) Å, the O(4)...0(16) distance being 4.211 Å. All this gives evidence for the existence of a large cavity between the two copper cations into which a suitable diatomic molecule can be inserted.

4.2 Electronic spectra

The sulfur-containing macrotricyclic compounds *189b*, *189d*, and *190b* form 1:2 ligand-copper(I) and ligand-copper(II) perchlorate complexes[294]. The complexes *189b*, *189d*, and *190b* with copper(I) ion are colorless, those with copper(II) ion are intensely violet, green, and blue, respectively. The addition of copper(II) perchlorate to *189b* in a ratio 1:1 gives first a green solution (λ_{max} 575 nm) and then, in a ratio of 2:1, a violet solution (λ_{max} 555 nm). The addition of one equivalent of copper(I) perchlorate and one equivalent of copper(II) perchlorate to the unsymmetric ligand of *190b* affords a mixed complex. The electronic spectra show that the Cu(I) and Cu(II) cations seem to be localized in the 18- and 12-membered rings of the macrocycle, respectively. So the interaction of *189b*, *189d*, and *190b* with Cu ions leads to the formation of binuclear cylindric macrotricyclic cryptates. The distances between the copper ions in the binuclear complexes *189b*, *189d*, and *190b* are 5.7 and 6.0 Å, respectively, as is evident from X-ray diffraction analysis. Thus, the macrocyclic cryptates synthesized have some free space for a molecule of appropriate size and binding ability to be inserted between the metal cations. The insertion of the molecule (O_2, N_2, etc.) between two metal cations in the binuclear complexes leads to cascade complexes possessing some interesting properties both in binuclear catalysis and in oxygen or nitrogen fixation.

IV. CONCLUSION

Oligomacrocycloalkanes The X-ray diffraction and spectroscopic data provide evidence that sulfur-containing macrocyclic ligands can assume both an *endo-* and an *exo*-conformation. Small transition metals form complexes of the *endo* type such as $NiL(BF_4)_2$ and $CuL(ClO_4)_2$ where the macrocycles are tetradentate and the complexes centrosymmetric square-planar tetragonal, respectively. With large ions [Co(III) and Rh(III)] the ligand remains *endo*-tetradentate, but the macrocycle undergoes bending which leads to a *cis*-geometry in complexes of the type *cis*-$[MLX_2]Y$ (X = halide ion, Y = monovalent ion). The macrocycle undergoes bending in those cases where its cavity is not large enough to allow the macrocycle to be coordinated to a metal in the planar conformation.

And, at last, in complexes of $HgCl_2$ with sulfur-containing macrocycles the ligand is turned inside out and exhibits an *exo* conformation. The coordination is achieved by two mercury ions, each being attached to two sulfur atoms. The remarkable flexibility

and variety of forms adopted by sulfur-containing macrocycles make them sharply different from nitrogen-containing analogs such as cyclame, for example, which exists predominantly in the *endo*-conformation. This seems to be partially due to the greater size of the releasing sulfur atoms in the ring which favors the formation of the *exo*-form. The ability of cyclame to form hydrogen bonds with its basic donating nitrogen atoms represents the main difference between these ligands. The investigation of the thermodynamics in solution has revealed that the hydrogen bonds are of great importance in complexing since they make the macrocyclic effect more pronounced for cyclame as compared with oligothiamacrocycles.[329]

Oligothiacyclophanes So, the important features of *158a*, *158c*, *158e*, and *158f* are that the bonds attached to the thiophene ring are displaced from its plane; the *O,S*-transoid conformation of the thenoyl fragment (*O,S*-cisoid conformation for compound *158e*), and the twist of the ketone group with respect to the thiophene ring. The valence angles at the methylene carbons are enhanced and the lactam groups display *trans*-configuration which favors a greater steric extension of the bridge. The above facts provide evidence for a conformation in which the *ansa*-bridge atoms are most distant from the thiophene ring π-electronic system, the valence bonds and torsion angles being least strained. In spite of all this, however, the molecules remain sterically hindered which leads to short transannular distances.[251]

Macroheterocycles containing polysulfide groups The study of the stereochemistry of hexathia[3.3]metacyclophanes has shown that conformational advantages are determined, first of all, by the nature of the trisulfide bridges. It is reported in the literature[330] that the polysulfide chains in polythionic compounds are arranged in such a conformation that the dihedral angles of adjacent sulfur atoms are within 74–110°. This is explained by repulsion of unpaired electron pairs of adjacent sulfur atoms for which the energy minimum is achieved at dihedral angles of 90°. The X-ray diffraction data of *179a* indicates that the C—S—S—S dihedral angles of this compound are close to 90°. On the other hand, the suggested *anti*-conformation for *179a* is scarcely probable since it requires the absence of dihedral C—S—S—S angles close to 90°. This interpretation supports the results of the reaction of mesitylene-2,4-dithiol with sulfur chlorides which leads exclusively to the formation of the unsymmetric metacyclophanes *178a* and *178b*. These date show that the *syn*-conformation in *178a* and *178b* does not seem possible due to reciprocal steric repulsion of the bulky substituents in positions 9 and 18. Therefore the compounds formed adopt the preferable *anti*-conformation in these cases.

Tricyclic systems Macrotricyclic ligands can form polynuclear cryptates including such with two or more metal cations in their intramolecular cavity. At present, these systems are of great interest as models of both polynuclear biological complexes and polynuclear catalysts. Introduction of a substrate (O_2, N_2, etc.) between two metal cations in binuclear complexes leads to cascade complexes. The addition of KO_2 or O_2 gives rise to the appearance of absorption bands at 330, 370, and broad absorption at 550–850 nm in the electronic spectra of 2Cu(II)*189b* and 2Cu(I)*189b*. These spectral

changes are possible when superoxides and oxygen are involved in the binuclear complex. Thus, the complexing of macrotricyclic ligands affords a new type of homo- and heteronuclear complexes of transition metals, potential bioinorganic models of biological processes (copper proteins, superoxide dismutation, etc.).

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