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Advances in the Chemistry of Sulphur-containing Macroheterocycles

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Data on the methods of synthesis and structures of macroheterocyclic sulphides as well as their complexes with alkali and transition metal ions are surveyed and described systematically.
The bibliography includes 185 references

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I. INTRODUCTION

The chemistry of macrocyclic compounds arose more than half a century ago as a result of the studies of Ruzicka, who synthesised macrocyclic ketones in order to discover the nature of the active principle of substances with the odour of musk[1,2]. The further development of this branch of organic chemistry was promoted by the fundamental studies of Ziegler[3-7], Hansley[8], Prelog[9], Stoll[10,11], Shemyakin[12-14], and others[15-18] carried out between 1930 and 1960.

At the present time, the chemistry of macrocyclic compounds is developing very vigorously, owing to the recently discovered extensive possibilities for the employment of macrocycles not only in chemical practice but also in biology, medicine and engineering[19-21]. The syntheses of catenanes and rotaxanes, crown-ethers and cryptands, cyclophanes, *ansa*-compounds, annulenes, etc. have attracted much attention.

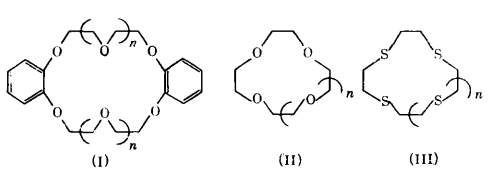
Macroheterocyclic compounds, namely crown-ethers, cryptands, and similar substances, whose study is closely related to the discovery of natural macroheterocyclic compounds, occupy a special place in the chemistry of macrocycles. The study of natural macroheterocycles—peptides, depsipeptides, and depsides—led to the discovery of their ability to form stable complexes with alkali and alkaline earth metals and to transfer these cations through natural and synthetic membranes. Such compounds have been called membranoactive complexones or ionophores[19]. The development of the chemistry of synthetic macroheterocyclic complexones is associated with the possibility of obtaining compounds whose properties are analogous to those of natural macroheterocycles. They can be regarded as simplified models of natural macroheterocyclic ionophores. Individual examples of synthetic macroheterocycles have been obtained by various groups of investigators[22-27], but the vigorous development of the chemistry of macroheterocycles has been stimulated by Pedersen's studies on the synthesis and complex formation reactions of macroheterocyclic polyethers with alkali and alkaline earth metal salts[28]. The vigorous development of the chemistry of macroheterocycles is indicated by the publication of recent monographs[19-21,29,30] and general reviews[31] and reviews devoted to individual classes of macroheterocycles: ethers[32], esters[33], amines[34], sulphides[35], heterocyclophanes[36], and other compounds of a similar type[37-40].

This review deals with studies on sulphur-containing macroheterocyclic compounds published in 1974–1980 (earlier investigations have been reviewed elsewhere[35]).

II. MACROHETEROMONOCYCLIC SULPHIDES

1. Macropolythiamonocyclanes

In 1967 Pedersen synthesised aromatic macroheterocyclic polyethers (I) and called them crown-ethers[28]. He observed that these compounds form stable complexes with alkali and alkaline earth metal cations as well as ammonium and silver cations. Crown-ethers are obtained by the condensation of 1,2-dihydroxyarenes with the corresponding α,ω-dichloro-derivatives in boiling 1-butanol in the presence of alkali metal hydroxides; in individual instances the yields reach 62%.

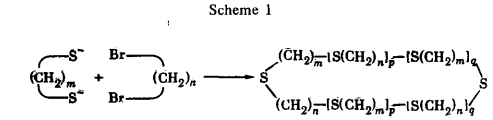


(I) (II) (III)

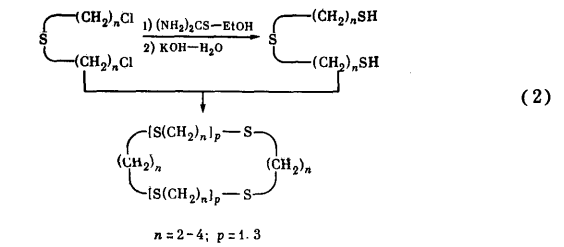
Instead of dichloro-derivatives, it is possible to employ ditosyl derivatives; heterocyclic polyethers of type (II) have been obtained from them in yields of 45%.[41-43,57] The high yields of crown-ethers can be accounted for by the "template" effect arising on coordination of alkali metal ions to the oxygen atoms in the cyclisation of the polyether.

Under analogous conditions, macropolythiamonocyclanes (III) are formed in only a low yield (less than 2%)[44] owing to the absence of the "template" effect because of the weak affinity of the sulphur atoms for alkali metal ions[45]. High dilution of the reaction mixture made it possible to improve the method of synthesis of macropolythiamonocyclanes[45,46]. The proposed methods (see Scheme 1) make it possible to synthesise macropolythiamonocyclanes in yields up to 35% (Table 1).

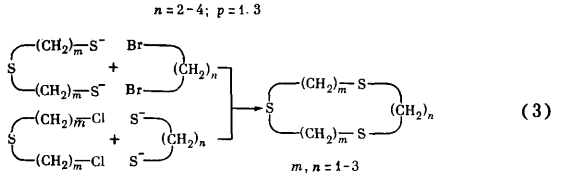
Scheme 1



$m, n = 3-5$; $p, q = 0,1$ (1)



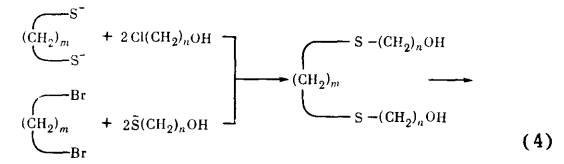
(2)



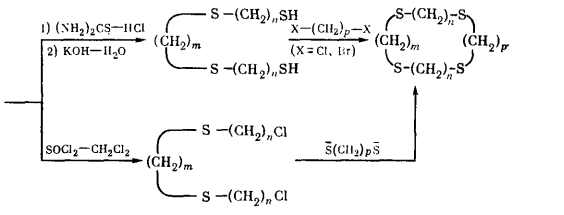
$n = 2-4$; $p = 1.3$

(3)

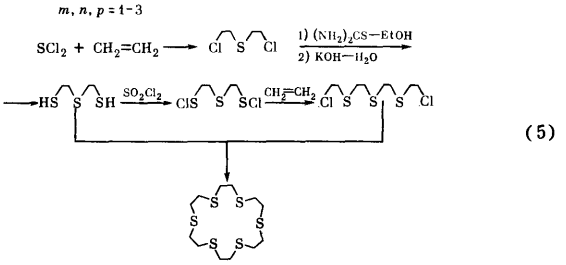
$m, n = 1-3$



(4)



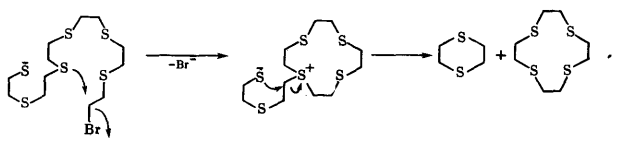
$m, n, p = 1-3$



(5)

Method (1) is most suitable for the synthesis of tetrathia- and hexathia-cyclanes in which the sulphur atoms are separated by tetra- and penta-methylene bridges. On the other hand, methods (3) and (5) lead to the maximum yields of macropolythiacyclanes consisting of alternating SCH_2CH_2 units.

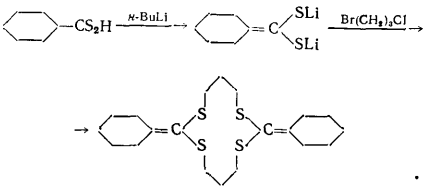
1,4-Dithiane and 1,4,7,10-tetrathiacyclododecane were unexpectedly obtained in reactions (1) and (3) together with 1,4,7,10,13,16-hexathiacyclo-octadecane. This is due to the formation of a cyclic sulphonium ion as a result of intramolecular cyclisation[45]:



When methods (2), (4), and (5) are used, the amount of side products is reduced to a minimum.

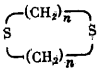
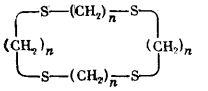
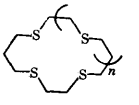
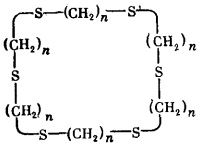
The kinetics of the formation of complexes by the Cu^{2+} ion with macrocyclic sulphides have been investigated and the influence of the solvent and the ring size has been considered[47-51]. The possibility of using these compounds as extractants for silver and mercury salts has been studied[52-55].

2,8-Bis(cyclohexylidene)-1,3,7,9-tetrathiacyclododecane (IV) has been obtained from cyclohexanedithiocarboxylic acid[56]:

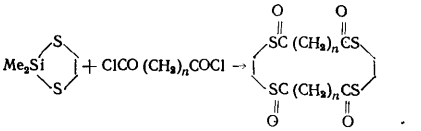


(IV)

Table 1. Macropolythiamonocyclanes.

Compound	n	M.p., °C	Yield, %	References
	5 6	81—82.5 77—78	0.8 1.4	[45] [45]
	3 4 5 6	57.5—59 31—32 33—33.5 30—32	19.5 3.9 5.3 3.9	[45, 49—51] [45, 51] [45] [45]
III	1 2 3	224—225 97.5—99 91—93	6.3 11.0 35.0	[45, 46, 49, 50] [45, 46, 49, 50] [45, 55]
	1 3 5	121—122.5 64—65 —	22.1 9.7 —	[45, 49—51, 53, 55] [45, 49] [53, 54]
	3 4 5 6	29—30 67—70 36.5—38 56—59.5	15.1 1.7 6.8 3.2	[45] [45] [45] [45]

The interaction of the highly reactive 2,2-dimethyl-2-sila-1,3-dithiacyclopentane with dicarboxylic acid dichlorides has been used to synthesise macroheterocyclic thiolactones (V):[57,58]



$n = 3, 5, 7, 8$ (V)

Several sulphur-containing annulenes have been obtained by the oxidative coupling reaction of diacetylenic sulphides[60, 61]. The interaction of bis[(triphenylphosphonia)methyl] sulphide dibromide with *o*-ethynylbenzaldehyde led to the synthesis of the corresponding diacetylenic derivative whose

oxidation in the presence of copper acetate in pyridine resulted in the formation of the macroheterocycle (VI):

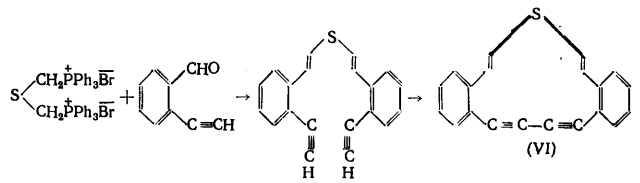
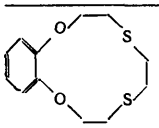
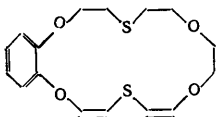
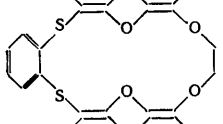
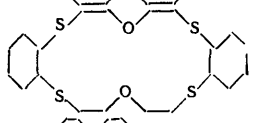
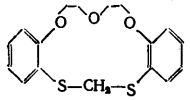
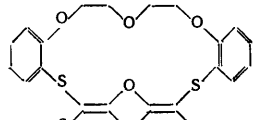
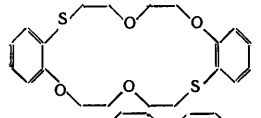
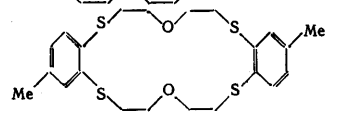
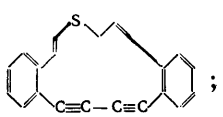


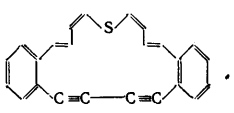
Table 2. Thiacrown-ethers.

Compound	M.p., °C	Yield, %
	92	34
	91	1.0
	*	56
	*	30
	150—153	3.0
	143—144	15
	113.5	5.0
	147	6.0

*An oil is formed.

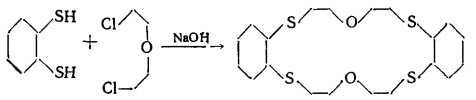
Compounds (VII) and (VIII) have been obtained analogously:


(VII)


(VIII)

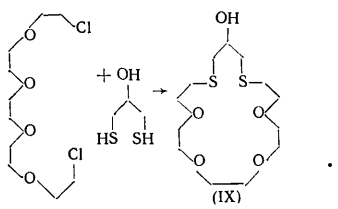
2. Macro-oxathiacyclanes

Crown-ethers containing sulphur atoms in the ring together with oxygen atoms were first synthesised by Pedersen[59,62], who also showed that, when oxygen atoms are substituted by sulphur atoms, the complex-forming properties of the crown-ethers in relation to potassium and sodium ions are weakened, while the complexes with silver ions are in fact strengthened. Thiacrown-ethers have been obtained by the condensation of aromatic 1,2-dithiols or *o*-mercaptophenol with aliphatic α,ω-dihalogeno-derivatives. The reaction of *o*-dihalogenoarenes with aliphatic α,ω-dithiols can also be used. *trans*-Cyclohexane-1,2-dithiol reacts with di(β-chloroethyl) ether analogous to 1,2-dithiols, forming 5,18-dioxa-2,8,15,21-tetrathiatricyclo[20,4,0,0^{9,14}]hexacosane:

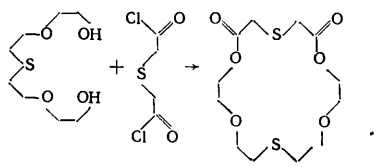


The thiacrown-ethers synthesised are listed in Table 2.[62]

The reaction of aliphatic α,ω-dithiols with dichlorohydrins has also been used to synthesise thiacrown-ethers (Table 3).[63] For example, the macroheterocycle (IX) has been obtained (in 80% yield) by the reaction of 1,14-dichloro-3,6,9,12-tetraoxatetradecane with 1,3-dimercapto-2-propanol:

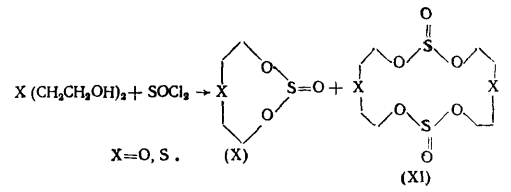


More than twenty thiacrown-ethers containing ester groups in the ring have also been obtained[64–68]. Sulphur-containing macroheterocyclic di- and tetra-oxa-esters have been synthesised by the interaction of oligo(ethylene thioglycols) or by the corresponding dithiols with the dichlorides of dicarboxylic acids under the conditions of high dilution (Table 3). The dichlorides of oxalic, malonic, succinic, and 3-thiaglutaric acids were used, for example:



Interest in macrolactones was aroused primarily by the possibility of using them as perfumes[33]. In connection with the discovery of the natural macrocyclic antibiotic valinomycin, containing carbonyl groups in the ring and exhibiting unique complex-forming properties in relation to alkali metal ions[19], nowadays these compounds attract attention as complex-forming agents. It was found that they exhibit a high complex-forming activity in relation to alkali and alkaline earth metal ions. Sulphur-containing macroheterocycles of this type form complexes with Na^+, K^+, Ag^+, Rb^+, Cs^+, and Ba^{2+} ions[69–72].

The reaction of diethylene glycol or β-thiodiglycol with thionyl chloride leads to the formation of heterocycles (X) of moderate size and macroheterocycles (XI):[73]



;

Table 3. Sulphur-containing di- and tetra-oxo-crown-ethers.

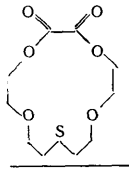
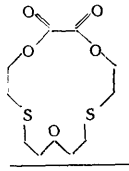
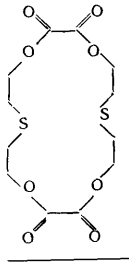
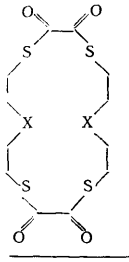
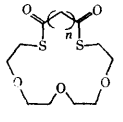
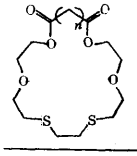
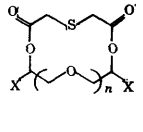
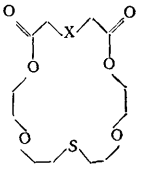
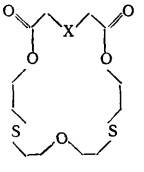
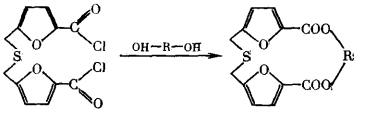
Compound	*n*	X	M.p., °C	Yield, %	Refs.
	—	—	88—90	5 7	[67]
	—	—	45	7.7	[67]
	—	—	195—203	14	[67]
	—	O	207—210	67	[67]
	—	S	108—109	62	[67]
	1	—	*	—	[64]
	2	—	*	—	[64]
	1	—	*	85	[64]
	2	—	*	80	[64]
	1	H	93.5—94.5	4.8	[65]
	2	H	85.5—86.5	2.3	[65]
	3	H	43.5—44.5	20	[65]
	1	Et	96.5—97.5	6	[68]
	2	Et	121.5—122.5	20	[68]

Table 3 (cont'd).

Compound	*n*	X	M.p., °C	Yield, %	Refs.
	—	O	113.5—115	35	[65]
	—	S	106—107	11	[65]
	—	O	36—36.5	20	[65]
	—	S	*	31	[65]

*An oil is formed.

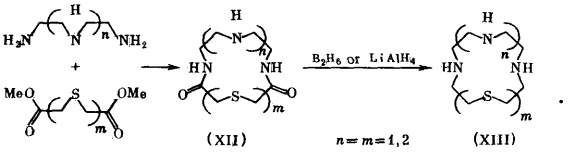
A series of sulphur-containing macroheterocycles have been synthesised using the dichloride of 5,5'-[thiobis(methylene)]-bisfuran-2-carboxylic acid as the key reagent[74]. A wide variety of diols (catechol, resorcinol, hydroquinone, monoethylene and triethylene glycols, 2,2-dimethylpropane-1,3-diol, propane-1,2-diol, 2,4-dimethyl-3-oxapentane-1,5-diol, *cis*- or *trans*-but-2-ene-1,4-diol, and but-2-yne-1,4-diol) as well as ethane-1,2-dithiol have been used as the second reagent (Table 4):



The reaction is carried out in the presence of lithium hydride in dimethylformamide with prolonged refluxing (20 h); the yields of the macroheterocycles are 11—77%.

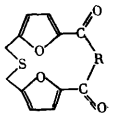
3. Macrothiazacyclanes

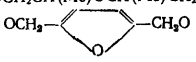
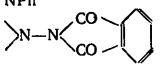
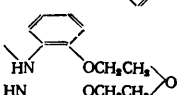
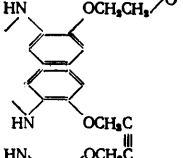
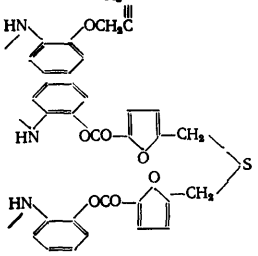
The general method of synthesis of macrothiazacyclanes is based on the aminolysis of the readily available dimethyl esters of thia-alkane-α,ω-dicarboxylic acids by polyethylenepolyamines and subsequent reduction of the resulting macroheterocyclic amides[75]:



Sulphur-containing macroheterocyclic diamides (XII) have been obtained in yields of 15.4—40.9% by heating the reactant for 3—7 days without high dilution or protection of the secondary amino-group. Successful cyclisation takes place by virtue of the different reactivities of the NH_2 and NH groups in the initial polyethylenepolyamines. The macrocyclic diamide can be reduced by lithium tetrahydroaluminate or diborane in tetrahydrofuran (THF), the yields of the corresponding macrothiazacyclanes (XIII) amounting to 60—80%.

Table 4. Macroheterocyclic derivatives of 5,5'-[thiobis-(methylene)]bisfuran-2-carboxylic acid.



R	M.p., °C	Yield, %	Refs.
$O(CH_2)_2O$	157—158	16	[74]
$[O(CH_2)_2]_3O$	212—214	54	[74]
$[O(CH_2)_2]_4O$	190—191	13	[74]
$[O(CH_2)_2]_5O$	215—217	28	[74]
$[O(CH_2)_2]_6O$	218—219	36	[74]
$O(CH_2)_2S(CH_2)_2O$	200—201	57	[74]
o-OC_6H_4O	46—48	77	[74]
m-OC_6H_4O	69—70	30	[74]
p-OC_6H_4O	66—68	11	[74]
$S(CH_2)_2S$	218—220	29	[74]
cis-$OCH_2CH{=}CHCH_2O$	192—193	70	[74]
trans-$OCH_2CH{=}CHCH_2O$	185—186	30	[74]
$OCH_2C{\equiv}CCH_2O$	216—218	60	[74]
$O(CH_2)_6O$	212—213	45	[74]
$OCH_2CH(Me)O$	185—186	53	[74]
$OCH(Me)CH(Me)O$	205—206	50	[74]
$OCH(Me)CH_2CH_2O$	214—215	65	[74]
$OCH_2C(Me)_2CH_2O$	216—217	52	[74]
$OCH_2CH(Me)OCH(Me)CH_2O$	218—220	37	[74]
	310—312	57	[87]
$OCH_2CH_2OCH_2C{\equiv}CCH_2OCH_2CH_2O$	218—220	43	[87]
$O(CH_2CH_2O)_2CH_2C{\equiv}CCH_2(OCH_2CH_2)_2O$	220—221	36	[87]
$O(CH_2CH_2O)_3CH_2C{\equiv}CCH_2(OCH_2CH_2)_3O$	217—218	12	[87]
trans-$OCH_2CH_2OCHCH{=}CHCH_2OCH_2CH_2O$	223—224	40	[87]
trans-$O(CH_2CH_2O)_2CH_2CH{=}CHCH_2(OCH_2CH_2)_2O$	210—211	32	[87]
$NH(CH_2)_2NH$	210—212	50	[86]
$NH(CH_2)_3NH$	72—73	22	[86]
$NH(CH_2)_8NH$	87—88	50	[86]
o-NHC_6H_4NH	197—198	97	[86]
m-NHC_6H_4NH	204—205	80	[86]
p-NHC_6H_4NH	224—225	91	[86]
$NH(CH_2)_2S(CH_2)_2NH$	45—46	93	[86]
NPh	184—185	97	[86]
	88—89	62	[86]
	230—231	53	[87]
	218—219	69	[87]
	225—227	83	[87]

Data on the synthesis of macroheterocycles containing alkyl, arylalkyl, or functional groups at the nitrogen or carbon atoms have been published with increasing frequency in recent years[32,40]. Such compounds have been used to form complexes with alkali and alkaline earth metal ions and to investigate complex formation kinetics, ion transfer through natural and synthetic membranes, and catalysis of interfacial transfer. Cryptands and their polymacroheterocyclic analogues have been synthesised from macroheterocycles with functional groups. Macroheterocycles with functional groups have been investigated as biologically active substances. After being immobilised in polymeric materials, such heterocycles are used as new heterogeneous catalysts. Finally they can be employed as reactive reagents in organic synthesis.

A new approach to the synthesis of open-chain and macroheterocyclic diamines with arylalkyl and functional group substituents has been discovered[76-80]. The synthesis of *N*-substituted open-chain diamines is based on the reaction of *N*-substituted aziridines with α,ω-dithiols. At 60 °C in methanol α,ω-dithiols react with two moles of aziridine, forming open-chain diamines (XIV). The analogous reaction in an aprotic solvent, for example, benzene, leads to the monoadducts (XV), which are oxidised by atmospheric oxygen to the corresponding disulphides (XVI) (Scheme 2):

Scheme 2

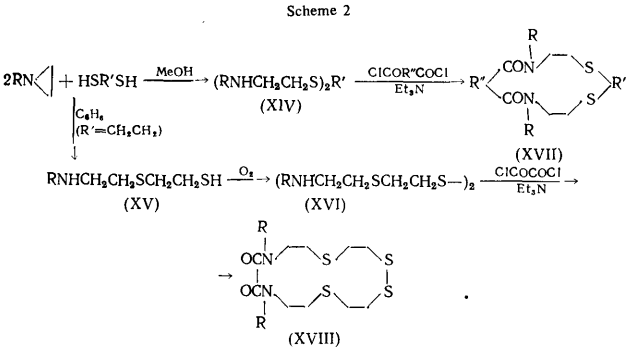
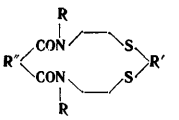
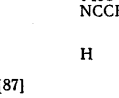
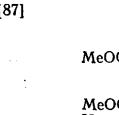


Table 5. Sulphur-containing macroheterocyclic diamides.



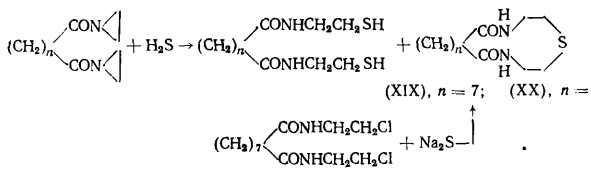
R	R'	R''	M.p., °C	Yield, %	Refs.
H	CH_2CH_2	$CH_2(CH_2)_2CH_2$	170—171	65	[80]
$PhCH_2CH_2$	CH_2CH_2	$CH_2(CH_2)_2CH_2$	134—135	70	[80]
$MeOCOCH_2CH_2$	CH_2CH_2	$CH_2(CH_2)_2CH_2$	105—107	68	[80]
$NCCH_2CH_2$	CH_2CH_2	$CH_2(CH_2)_2CH_2$	184—185	70	[80]
H	CH_2CH_2	*o*-C_6H_4	181—182	66	[76—78]
$PhCH_2CH_2$	CH_2CH_2	*o*-C_6H_4	190—191	70	[80]
$MeOCOCH_2CH_2$	CH_2CH_2	*o*-C_6H_4	*	70	[76—78]
$NCCH_2CH_2$	CH_2CH_2	*o*-C_6H_4	*	70	[80]
H		*o*-C_6H_4	135—136	50	[79]
$MeOCOCH_2CH_2$		*o*-C_6H_4	72—73	55	[79, 80]
$MeOCOCH_2CH_2$	CH_2CH_2	$CH_2CH_2SCH_2CH_2SCH_2CH_2$	*	60	[80]
H	$CH_2CH_2SSCH_2CH_2$	—	135	80	[76—78]
$MeOCOCH_2CH_2$	$CH_2CH_2SSCH_2CH_2$	—	*	60	[80]

*An oil is formed.

The cyclisation of the diamines (XIV) and (XVI) with dicarboxylic acid dichlorides has been investigated with the aim of synthesising macroheterocyclic compounds containing arylalkyl and functional groups at the nitrogen atom. The reaction is carried out in dry benzene at high dilution. The resulting *N*-unsubstituted macroheterocycles as well as the macroheterocyclic compounds (XVII) and (XVIII), containing

phenylethyl, methoxycarbonylethyl, and cyanoethyl groups are presented in Table 5.

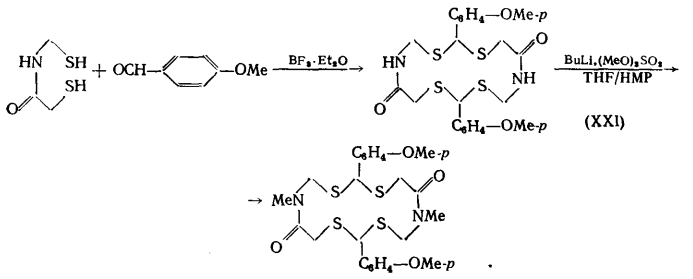
The reaction of bis-*N*-ethyleneamides of azelaic and sebacic acids with an excess of hydrogen sulphide led to the isolation of the macrocyclic sulphides (XIX) and (XX) together with the bis(β-mercaptoethyl)diamides of the corresponding dicarboxylic acids[81]:



(XIX), $n = 7$; (XX), $n = 8$

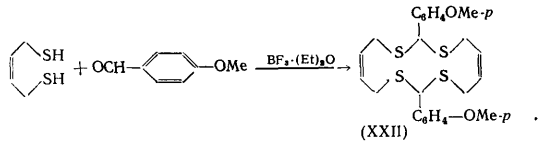
The macrocyclic compounds are apparently the products of the intramolecular opening of the aziridine rings by the mercapto-group in the intermediate *N*,*N*-ethylene-*N*'-(β-mercaptoethyl)diamides of azelaic and sebacic acids. The cyclic sulphide (XIX) has also been synthesised by the reaction of the bis(β-chloroethyl)diamide of azelaic acids with sodium sulphide.

The reaction of the *N*-(mercaptomethyl)amide of thioglycolic acid with anisaldehyde leads to the formation of the macrocycle (XXI):[82]



(XXI)

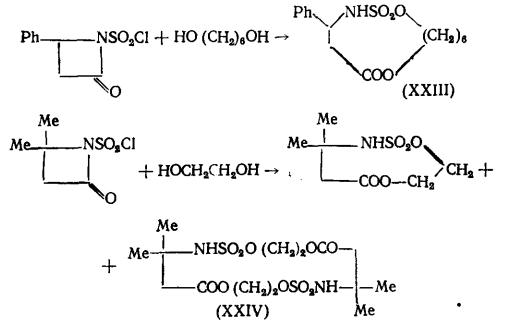
The macroheterocycle (XXII) has been obtained analogously by the reaction of 1,4-dimercaptobut-2-ene with anisaldehyde:



(XXII)

4. Macro-oxathiazacyclanes

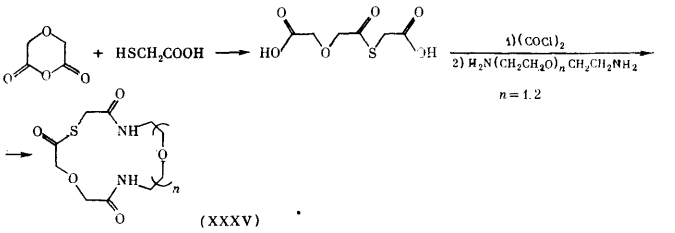
The reaction of *N*-chlorosulphonyl-β-lactams with glycols leads to the formation of the new macroheterocycles (XXIII) and (XXIV):[83–84]



(XXIII)

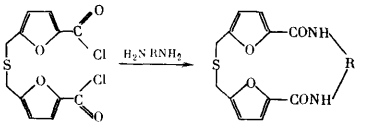
(XXIV)

Oxygen- and nitrogen-containing macroheterocyclic sulphides have been synthesised from 5-oxo-3-oxa-6-thiahexanedicarboxylic acid, which is the product of the reaction of the anhydride of diglycolic acid with thioglycolic acid[85]. The dicarboxylic acid obtained was converted by treatment with oxalyl chloride into the corresponding acid dichloride whose reaction with 1,5-diamino-3-oxapentane or 1,8-diamino-3,6-dioxaoctane at high dilution leads to the macroheterocycle (XXXV) in 30–35% yield:

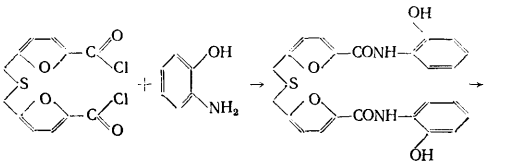


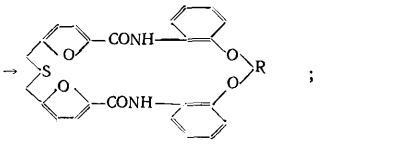
(XXXV)

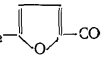
The macroheterocyclic amides have been obtained analogously in higher yields using the dichlorides of 5,5'-[thiobis(methylene)]bisfuran-2-carboxylic acid and aliphatic or aromatic diamines (Table 4):[86]



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





R=$CH_2CH_2OCH_2CH_2$, $CH_2C{\equiv}CCH_2$, CO––CH_2SCH_2––CO

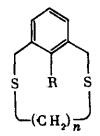
The reaction of the dichloride of 5,5'-[thiobis(methylene)]-bisfuran-2-carboxylic acid with o-aminophenol leads to the corresponding diamide, whose subsequent interaction with dichlorides (refluxing in the presence of potassium hydroxide for 25–30 h) leads to the formation of sulphur-containing macroheterocycles in 53–83% yields (Table 4).[87]

III. THIA- AND POLYTHIA-CYCLOPHANES

1. Sulphur-containing Cyclophanes

Cyclophanes are cyclic compounds containing one or several benzene rings connected by polymethylene bridges in the *ortho*-, *meta*-, or *para*-positions. Interest in these compounds arose in connection with the possibility of investigating the steric interaction of substituents, transannular effects, the dependence of the barrier to the rotation of the benzene rings on the length of the methylene bridge, etc.

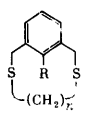
A large series of dithiacyclophanes (XXVI), containing from 3 to 12 methylene groups in each aliphatic bridge incorporating a wide variety of intra-annular substituents in the benzene ring, have been synthesised (Table 6).



(XXVI)

n=3–12; R=Ph, I, NH_2, NO_2, OH, OMe, SMe, SOMe, SO_2Me

Table 6. Dithiametacyclophanes

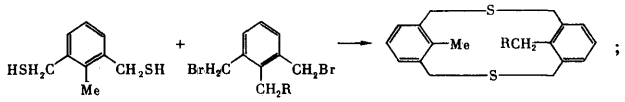


n	R	M.p., °C	Yield, %	Refs.	n	R	M.p., °C	Yield, %	Refs.
3	NO_2	145—148	4	[88]	8	CO_2Me	80—82	34	[88]
4	NO_2	102	45	[88]	9	CO_2Me	*	39	[88]
5	NO_2	97	21	[88]	10	CO_2Me	*	57	[88]
6	NO_2	116	42	[88]	11	CO_2Me	*	46	[88]
7	NO_2	94	20	[88]	12	CO_2Me	*	49	[88]
8	NO_2	80	48	[88]	4	SMe	100—103	3	[88]
9	NO_2	41—43	13	[88]	6	SMe	101—104	15	[88]
10	NO_2	78—80	2	[88]	8	SMe	*	44	[88]
8	I	44—47	17	[91]	9	SMe	*	53	[88]
9	I	<20	9	[91]	10	SMe	*	38	[88]
10	I	<20	11	[91]	4	SOMe	154—156	29	[89]
6	OH	113—114	4	[91]	6	SOMe	148—150	38	[89]
7	OH	108—110	5	[91]	8	SOMe	128—130	19	[89]
4	NH_2	94—95	39	[91]	9	SOMe	124—125	37	[89]
5	NH_2	76—77	56	[91]	10	SOMe	112—114	22	[89]
6	NH_2	79—80	67	[91]	11	SOMe	97—100	11	[89]
7	NH_2	77—78	60	[91]	4	SO_2Me	144—147	5	[88]
8	NH_2	42—44	55	[91]	6	SO_2Me	118—120	29	[88]
9	NH_2	<—16	73	[91]	8	SO_2Me	177—180	11	[88]
6	NHAc	161—164	60	[91]	10	SO_2Me	154—156	10	[88]
8	NHAc	110	98	[91]	11	SO_2Me	128—130	19	[88]
9	NHAc	90—91	89	[91]	12	SO_2Me	80—82	18	[88]
8	$N(Ac)_2$	126	94	[91]	4	Ph	133—134	22	[88]
9	$N(Ac)_2$	110—111	96	[91]	5	Ph	109—110	23	[88]
6	CO_2Me	102—103	30	[88]	6	Ph	126—127	9	[88]
					7	Ph	*	22	[88]
					8	Ph	62—64	18	[88]
					10	Ph	44—46	11	[88]
					12	Ph	*	11	[88]

*An oil is formed.

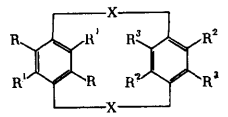
Cyclophanes with oxygen and sulphur atoms in the polymethylene bridges have also been obtained[88–91,111,117]. It has been shown by NMR that the steric requirements of an NO_2 group in these macrocyclic compounds are somewhat less stringent than those of a methyl group. CO_2Me and SO_2Me Groups are more bulky than NO_2 and SMe, but the bulk of an SMe group is greater than that of an OMe group. An SOMe group occupies an intermediate position between SO_2Me and SMe; the bulk of an NH_2 group is similar to that of a hydroxy-group. Both these substituents (NH_2 and OH) are more bulky than a fluorine atom linked to the aromatic ring, but are appreciably smaller than a chlorine atom or SMe and NO_2 groups. The general steric requirements of an iodine atom linked to an aromatic ring are more stringent than those of a chlorine or bromine atom but are comparable to those of an SMe group[88–91].

Dithiametacyclophanes containing intra-annular alkyl, alkenyl, and alkoxy-groups in the benzene ring have been synthesised[92,93]. They have been obtained by the interaction of 2,6-bis(mercaptomethyl)toluene with 2,6-bis(bromomethyl)-substituted benzenes; the yields of the macroheterocycles (XXVII) are 53–80%:



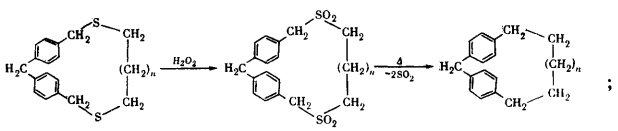
R = n-Pr, $CH_2CH{=}CH_2$, CH_2OMe. (XXVII)

Dithiaparacyclophanes containing bromine atoms, methoxy-groups, or cyano-groups in the benzene ring have been synthesised by the reaction of the corresponding 1,4-bis-(mercaptomethyl)benzenes with 1,4-bis(bromomethyl)-benzenes[94,95]:



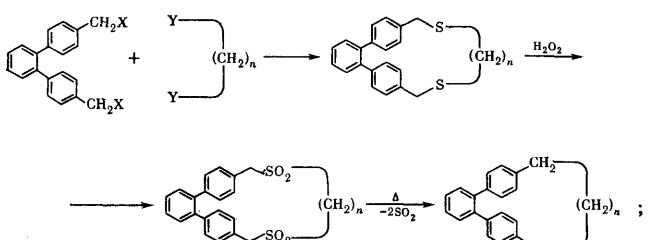
X = S, SO_2; R = R^1 = R^2 = R^3 = H; X = S, SO_2; R = R^2 = H, R^1 = CN, R^3 = OMe; X = S, SO_2; R = R^3 = H, R^1 = CN, R^2 = OMe; X = S; R = Br, R^1 = R^3 = OMe, R^2 = H .

In recent years the pyrolysis of cyclic sulphones has been used widely for the synthesis of cyclophanes. The synthesis of sterically hindered paracyclophanes (XXVIII) has been achieved in this way[96]:



n=1–3. (XXVIII)

A series of cyclophanes containing two or three benzene rings in their molecules has been obtained[97–101]. The main method of synthesis of the initial dithiacyclophanes involves the reaction of the corresponding dibromides with dithiols (Table 7):

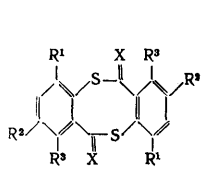


n=2–10, X=Br, SH, Y=SNa, Br .

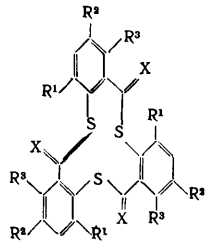
An analogous method has been used to synthesise dithiabiphenylophanes[102–105], dithiabiphenylnaphthalinophanes[123–131], dithiaphenanthrenophanes, and dithiaphenanthrenonaphthalinophanes[136–138] (Table 8).

The homocyclisation of o-mercaptobenzyl chloride under the influence of sodium hydroxide and of methyl-substituted o-mercaptobenzoic acids under the influence of P_5O_{10} at a high

dilution proceeds with formation of both cyclic dithiaorthocyclophanes (XXIX) of moderate size and the macrocyclic trithiaorthocyclophanes (XXX) (yield 6.4–10%).[107,116,122]



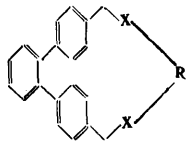
(XXIX)



(XXX)

$X = H_2$, $R^1 = R^2 = R^3 = H$; $X = O$, $R^1 = Me$, $R^2 = R^3 = H$;
$X = O$, $R^1 = R^3 = H$, $R^2 = Me$;
$X = O$, $R^1 = R^2 = H$, $R^3 = Me$; $X = O$, $R^1 = R^3 = Me$, $R^2 = H$.

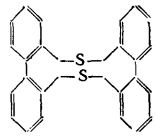
Table 7. Dithiatriphenylenophanes[98]



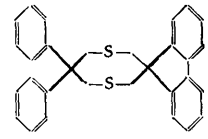
R	M.p., °C	Yield, %	M.p., °C	Yield, %
	X=S		X=SO$_2$	
$CH_2CH_2OCH_2CH_2$	157—159	14	297—299	90
$CH_2(CH_2OCH_2)_2CH_2$	117—118	19	232—234	60
$CH_2(CH_2OCH_2)_3CH_2$	110—112	7	235—238	87
$CH_2CH_2SCH_2CH_2$	110—111	9	—	—
$CH_2CH_2SO_2CH_2CH_2$	—	—	330—332	80
o-$CH_2C_6H_4CH_2$	192—195	12	355*	80
m-$CH_2C_6H_4CH_2$	175—177	17	323—324	73
2-$CH_2C_6H_3(NO_2)CH_2$-6	190—193	9	295*	74
2-$CH_2C_6H(Me_3$-1,3,5$)CH_2$-6	241—242	19	350*	80
p-$CH_2C_6H_4CH_2$	172—175	17	337—338	82

*Decomposition temperature.

The cyclocondensation of $(o\text{-}BrCH_2C_6H_4)_2$ with $(o\text{-}HSCH_2C_6H_4)_2$ leads to the formation of a mixture of the sulphur-containing macroheterocycles (XXXI) and (XXXII):[108]



(XXXI)



(XXXII)

Table 8. Sulphur-containing biphenylo-, naphthaleno-, and anthraceno-phanes.

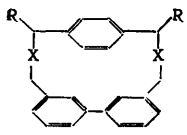
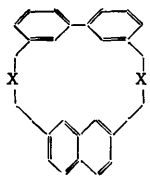
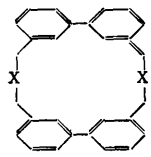
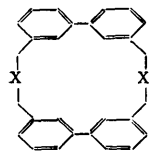
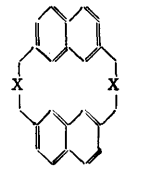
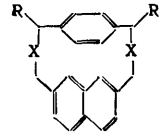
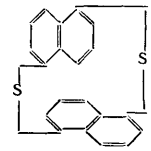
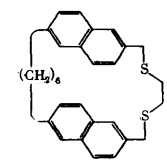
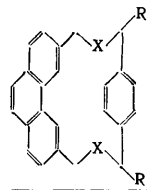
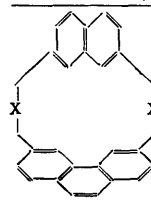
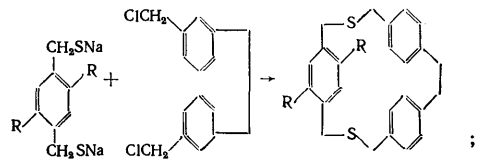
Compound	X	R	M.p., °C	Yield, %	Refs.
	S	H	213—215	49	[102]
	S	Me	180—181	63	[102]
	SO_2	H	>300	100	[102]

Table 8 (cont'd).

Compound	X	R	M.p., °C	Yield, %	Refs.
	S	—	234—235	49	[103, 123]
	$^+SMeBF_4^-$	—	>300	—	[103, 123]
	SO_2	—	>350	—	[103]
	S	—	266—268	74	[104]
	$^+SMeBF_4^-$	—	>300	—	[104]
	SO_2	—	>300	—	[104]
	S	—	249—251	73	[105]
	$^+SMeBF_4^-$	—	205—207*	~100	[105]
	SO_2	—	320	95	[105]
	S	—	240—244	—	[124, 137]
	$^+SMeBF_4^-$	—	>210	93	[124]
	SO_2	—	>300	89	[124]
	S	H	239—241	50	[125, 126]
	S	Me	245—246	55	[125, 126]
	$^+SMeBF_4^-$	H	>340	~100	[125, 126]
	$^+SMeBF_4^-$	Me	>360	~100	[125, 126]
	SO_2	H	>340	97	[125]
	—	—	281—283	6	[129]
	—	—	190—192	56	[131]
	S	H	248—250	52	[136, 137]
	$^+SMeBF_4^-$	H	>300	~100	[137]
	SO_2	H	>300	26	[137]
	S	Me	208—210	36	[137]
	$^+SMeBF_4^-$	Me	300*	90	[137]
	S	—	249—250	60	[138]
	$^+SMeBF_4^-$	—	>300	94	[138]

*Decomposition temperature.

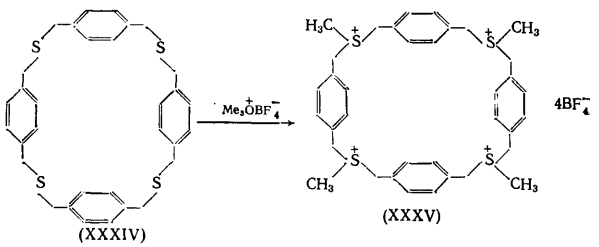
In order to investigate the effects of the internal rotation of the benzene rings in macrocyclophanes, dithiatriparacyclophanes (XXXIII) with various substituents in the *para*-position of the benzene ring have been obtained[109]:



R = H, F, Cl, Me, OMe . (XXXIII)

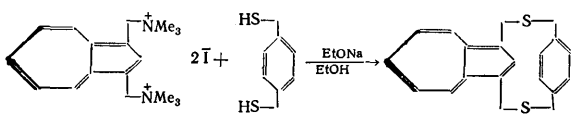
They were synthesised by the reaction of sodium dithiolates with 1,2-bis(4-chloromethylphenyl)ethane in a benzene-alcohol solution at high dilution; the yields of the dithiacyclophanes (XXXIII) are 15–55%.

When the tetrasulphide (XXXIV) was treated with $Me_3\overset{+}{O}\overline{B}F_4$, the water-soluble tetrathiaparacyclophane (XXXV) was isolated[110]:



(XXXIV) (XXXV)

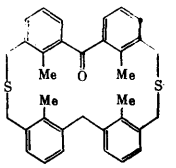
Using the high dilution technique, dithia-azulenoparacyclophane (XXXVI) was synthesised by the reaction of 1,3-bis(trimethylammoniamethyl)azulene di-iodide with 1,4-bis(mercaptomethyl)benzene (yield 40%):[114]



(XXXVI)

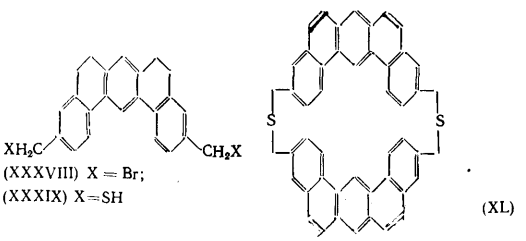
Two-layer and three-layer cyclophanes have been obtained in order to investigate the transannular interaction between the π electrons of the benzene ring[106,112,113,118–120,149]. The method of their synthesis is based on the pyrolysis of bis-sulphones or the photoextrusion of sulphur from bis-sulphides. The three-layer paracyclophanes are presented in Scheme 3.

Tetramethyldithiametacyclophane (XXXVII) has been obtained by the cyclisation of bis(3-bromomethyl-2-methyl)-benzophenone with bis(3-mercaptomethyl-2-methylphenyl)-methane in 80% yield[121]:



(XXXVII)

Sulphur-containing anthraceno- and anthraquinononophanes and pentaphenyleno-phanes have been described[132–135]. Dithiadibenzanthracenophane (XL) has been obtained by the reaction of bis(bromomethyl)dibenzanthracene (XXXVIII) with bis(mercaptomethyl)dibenzanthracene (XXXIX) (yield 55%):[139]

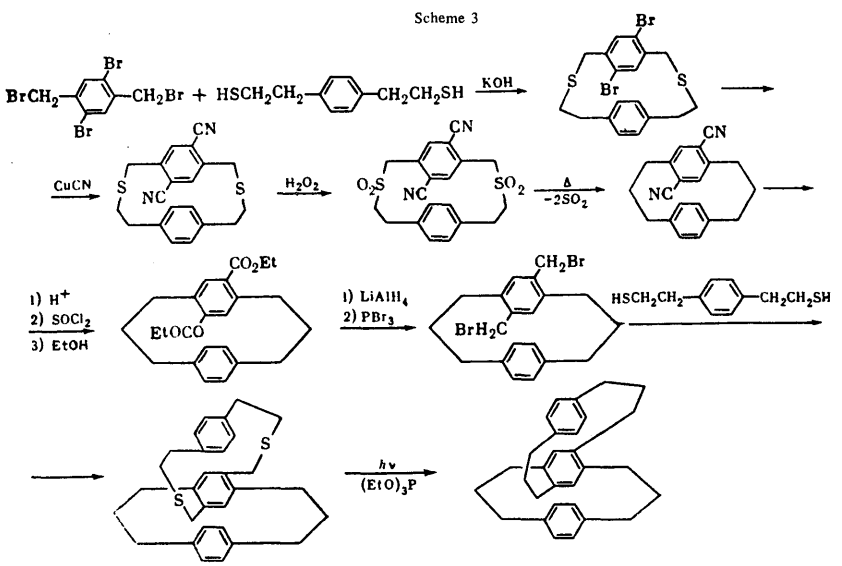


(XXXVIII) X = Br;
(XXXIX) X = SH (XL)

2. Thiophenophanes

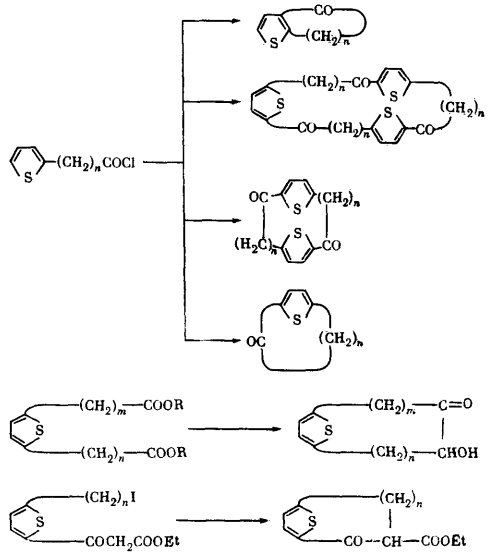
A method based on the intramolecular and intermolecular acylation of the chlorides of ω-thienylalkanecarboxylic acid, the acyloin condensation of 2,5-bis(alkoxycarbonylalkyl)-thiophens, and the intramolecular alkylation of ω-halogenoalkyl-substituted β-ketoesters of the thiophen series have

Scheme 3



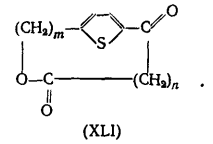
been developed for the synthesis of macrocyclic compounds incorporating the thiophen ring[29,140,144,145,150–152,155,156] (Scheme 4).

Scheme 4



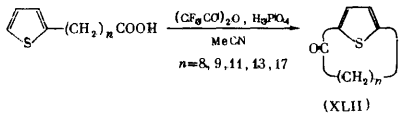
These investigations have been reviewed[35].

The X-ray diffraction determination of the geometrical and conformational parameters of the isomeric *ansa*-ketolactones having the general formula (XLI) and incorporating the thiophen ring[141–143,146–148] made it possible to explain the different ease of formation of macrocyclic ketolactones depending on the position of the ester group in the *ansa*-bridge and also the characteristics of their spectra and physical and chemical properties:



(XLI)

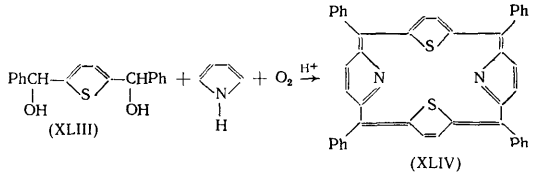
(2,5)-Thiophenophan-1-ones (XLII) have been synthesised by the cyclisation of ω-(2-thienyl)alkanecarboxylic acids in the presence of 85% phosphoric acid and trifluoroacetic anhydride in dry acetonitrile[153,154]:



(XLII)

The yields of the macrocycles (XLII) increase from 9 to 66% with increase of the length of the polymethylene bridge.

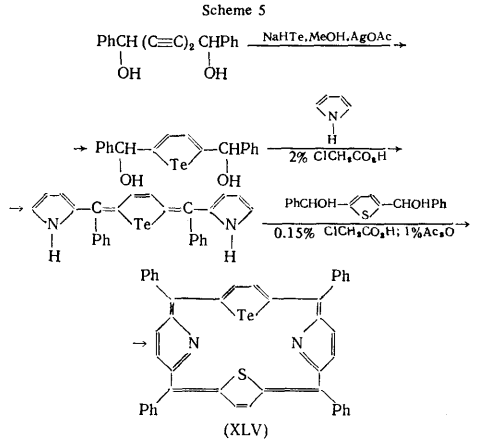
Tetraphenyl-21,23-dithiaporphyrin (XLIV) has been obtained by the reaction of 2,5-bis(α-hydroxybenzyl)thiophen (XLIII) with pyrrole (yield 10%):[157]



(XLIV)

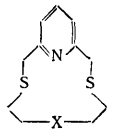
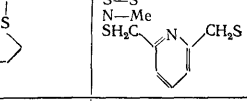
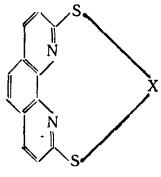
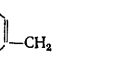
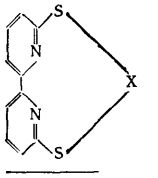
A new tetraphenylporphyrin (XLV), containing sulphur and tellurium atoms together with nitrogen atoms, has been synthesised by the following scheme[185].

Scheme 5



(XLV)

Table 9. Sulphur-containing pyridinophanes.

Compound	X	M.p., °C	Yield, %	Refs.
	S	162—163	50	[158]
	SO	171—174	26	[158]
	SCH_2CH_2S	131—133	38	[158]
	S—S	151—153 *	13	[158]
	N—Me	67—69	11	[158]
	SH_2C  CH_2S	213—216 **	19	[158]
	$CH_2CH_2SCH_2CH_2$	263	—	[160]
	$CH_2CH_2OCH_2CH_2OCH_2CH_2$	197	—	[160]
	$CH_2CH_2SCH_2CH_2SCH_2CH_2$	173	—	[160]
	$CH_2CH_2(OCH_2CH_2)_3$	127	—	[160]
	$(CH_2)_6$	156	—	[160]
	$(CH_2)_8$	125	—	[160]
	$H_2C—C_6H_4—CH_2$	210	—	[160]
		281	—	[160]
	$(CH_2)_8$	71	—	[160]
	$CH_2CH_2(OCH_2CH_2)_3$	205	—	[160]

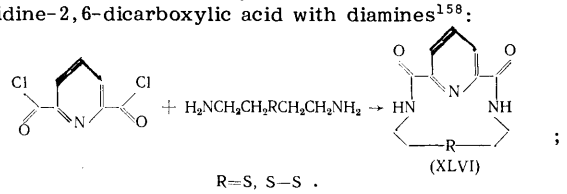
*Sublimation.

**Decomposition temperature.

3. Sulphur-Containing Pyridinophanes

Pyridinophanes have been synthesised by the reaction of 2,6-bis(bromomethyl)pyridine with various α,ω-dithiols (Table 9). The pyridinophanes (XLVI) containing diamide

groups have been obtained by the reaction of the dichloride of pyridine-2,6-dicarboxylic acid with diamines[158]:



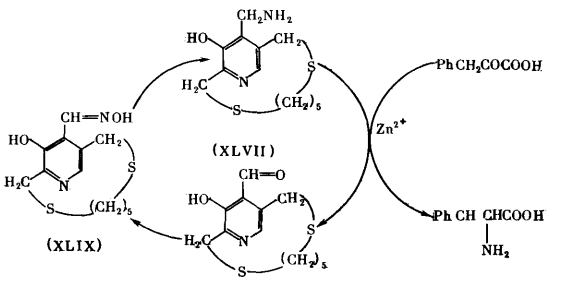
(XLVI)

R=S, S—S .

The sulphur-containing pyridinophanes synthesised 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+} (yields 39–96%).

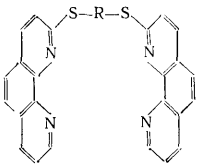
(−)-15-Aminomethyl-14-hydroxy-2,8-dithia[9](2,5)-pyridinophane (XLVII) has been used as a transaminating agent in the reaction with phenylpyruvic acid[115,159]. Zinc salts have been used as catalysts. Pyridoxamine (XLVII) has been obtained from the pyridinophane (XLVIII) by treatment with NH_2OH–HCl–AcOna–EtOH and subsequent reduction of the oxime (XLIV) with $NaBH_2S_3$ in THF. The transamination reaction is carried out by stirring a mixture of the pyridinophane (XLVII), sodium phenylpyruvate, and $ZnClO_4 . 6H_2O$ at room temperature for 20 h in acetonitrile (Scheme 6); the maximum yield of phenylalanine is 83%:

Scheme 6



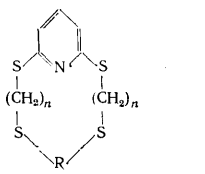
(XLVIII)

Macroheterocyclic phenanthrolines and dipyrinide (Table 9), in which the bridging sulphur atoms are linked directly to the pyridine ring, have been synthesised by the reaction of 2,9-dichloro-1,10-phenanthroline and 6,6′-dichloro-2,2-bipyridyl with α,ω-dithiolates in 3-methyl-1-butanol[160]. These macroheterocycles do not form crystalline complexes with alkali metal or alkaline earth metal ions, while among heavy metal ions complexes are formed only with silver and mercury ions. The open-chain ligands (L)–(LII) used for comparison readily form complexes with Co^{2+}. It has been suggested that the weak coordinating capacity of the macroheterocyclic ligand synthesised is associated with the shielding effect of the bridging chains[160].



(L) R=$CH_2CH_2XCH_2CH_2$ (X=O, S);
(LI) R=$CH_2(CH_2)_nCH_2$ (n = 3, 4, 9);

(LII) R=



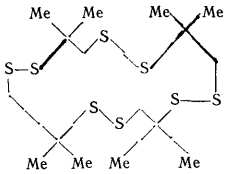
(LIII) n = 2, R=CH_2CH_2;

(LIV) n = 4, R=

The pyridinophanes (LIII) and (LIV) have been obtained by the reaction of 2,6-dihalogenopyridines with α,ω-dithiols[161].

IV. MACROHETEROCYCLIC DI- AND POLY-SULPHIDES

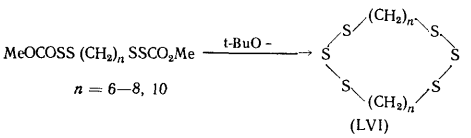
The synthesis of the 16-membered polydisulphide (LV) by treating the isobutene–sulphur monochloride adduct with a solution of sodium hydrogen sulphide has been described[162].



(LV)

The same substance is formed by the reaction of 2-chloro-2-methylpropyl disulphide, methylallyl disulphide, or sodium methylallyl thiosulphate with sodium hydrogen sulphide; the maximum yield of compound (LV) is 45%.

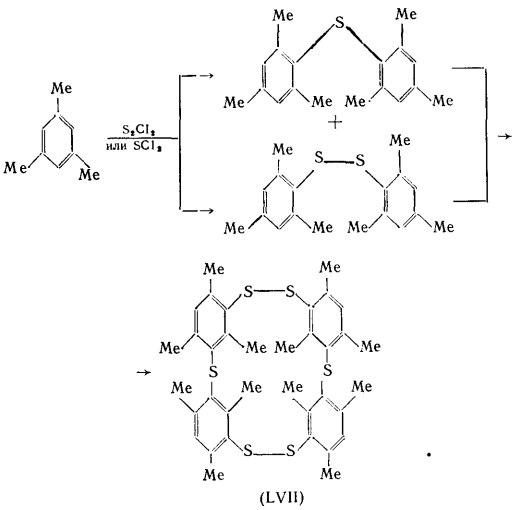
Macroheterocyclic trisulphides have also been formed as a result of the decomposition of polymethylenebis-sulphenyl thiocarbonates by alkoxides[163]:



(LVI)

The yields of the trisulphides (LVI) increases with increase of the length of the bis-sulphenyl thiocarbonate chain. Thus the yields are 16, 22, 50, and 86% respectively for n = 6, 7, 8, and 10.

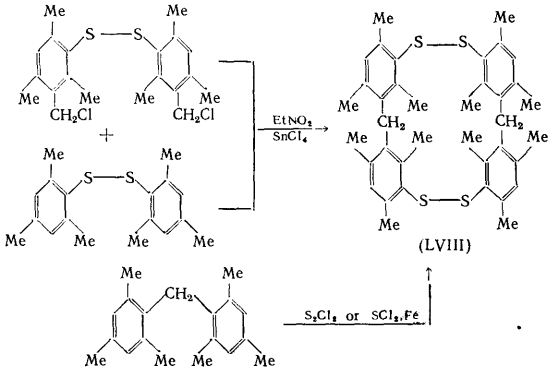
The synthesis of the polythiamacroheterocycle (LVII) has been achieved by the direct introduction of sulphur into mesitylene with the aid of sulphur monochloride or dichloride[164]:



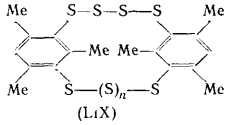
(LVII)

The reaction takes place when the mixture of the reactants is refluxed in chloroform in the presence of iron powder. When sulphur monochloride is used, the yield of compound (LVII) reaches 18%, while in the reaction with sulphur dichloride it does not exceed 3%. The interaction of dimesitylmethane with sulphur monochloride has been studied under analogous conditions and tetrathia[2,1,2,1]metacyclophane (LVIII) with alternating disulphide and methylene linkages

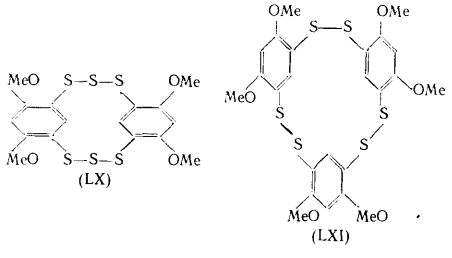
was isolated (yield 15%); in the reaction with sulphur dichloride, compound (LVIII) is formed in 3% yield[165]:



The formation of asymmetric macroheterocyclic polysulphides (LIX) in the reaction of mesitylene-2,4-dithiol with sulphur chlorides was entirely unexpected[166]. Their structure was confirmed by X-ray diffraction and NMR measurements:

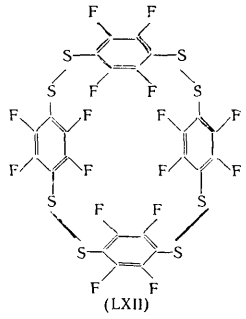


The interaction of 1,3-dimethoxybenzene with sulphur chlorides, catalysed by iron, has been studied at normal dilution and using a high dilution technique[167–169]. In the former case, linear polysulphides were obtained, while under the conditions of high dilution a mixture of two macroheterocycles, (LX) and (LXI), is formed in yields of 6 and 1.5% respectively:



One of the methods of synthesis of macroheterocyclic polysulphides involves the oxidation of dithiols. It was stated previously that the oxidation of benzene-1,4-dithiols leads to the formation of polymeric disulphides[170–172]. However, macroheterocyclic compounds have been synthesised on treatment with iodine at high dilution in 30% yield[173]. The oxidation of naphthalene-1,4-dithiol in the presence of alkali metal hexacyanoferrates(III) also leads to a macroheterocyclic compound[174].

The oxidation of tetrafluorobenzene-1,4-dithiol in diphenyl sulphoxide yielded the macroheterocyclic tetrakisdisulphide (LXII) in 95% yield[175]. The ease of conversion of tetrafluorobenzene-1,4-dithiol into the macrocyclic polysulphide (LXII) is unique. On the other hand, when an attempt was made to oxidise benzene-1,4-diothiol, 2,5-dimethoxybenzene-1,4-dithiol, and tetramethylbenzene-1,4-dithiol under analogous conditions, only polymeric products were isolated. The oxidation of tetrachlorobenzene-1,4-dithiol has been investigated but the molecular weight of the entire product synthesised could not be determined owing to its low volatility and solubility[175].

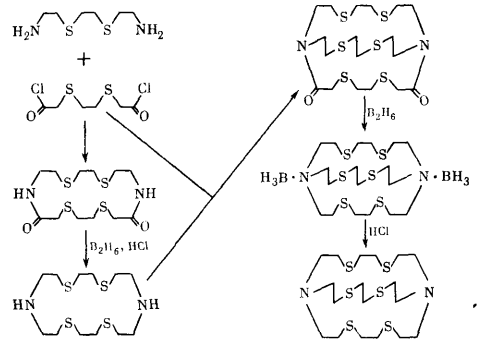


V. MACROHETEROBICYCLIC AND MACROHETEROTRICYCLIC SULPHIDES

In 1969 Dietrich et al.[176,177] synthesised a series of macrobicyclic polyaminoethers which have been called cryptands. The main characteristic of compounds of this type is the stability of their complexes with a wide range of cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, etc.). Cryptates—the complexes of macrobicyclic polyaminoethers—are readily soluble in water and organic media and their stability is superior to that of the complexes with macromonocyclic polyaminoethers.

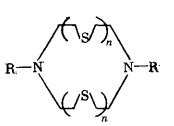
Sulphur-containing cryptands have been obtained in the following way (Scheme 7).[178] The corresponding dichlorides of oxa- or thia-dicarboxylic acids were condensed with 1,8-diamino-3,6-dithiaoctane at high dilution. The diamides isolated were reduced with diborane and, after hydrolysis with hydrochloric acid, were converted into monocyclic diamines. The latter were again condensed with dicarboxylic acid dichlorides and the bicyclic diamides formed were converted, like the monocyclic compounds, into macrobicyclic sulphur-containing polyaminoethers (Scheme 7):

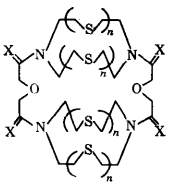
Scheme 7

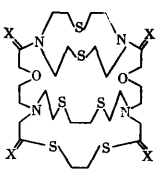


Macropolycyclic ligands can form polynuclear cryptates by incorporating two or more metal cations in the inner cavity within the molecule. Such systems are at present of great interest as models of polynuclear biological complexes and also as polynuclear catalysts. A general synthetic method has been developed[183,184] for the construction of cylindrical macrotricyclic systems which contain rings with different numbers of heteroatoms and different sizes of the inner cavity and a study has been made of their complex formation reactions with univalent and bivalent copper salts.

The sulphur-containing tetra-amide (LXX) has been synthesised by condensing the macroheterocycle (LXVI), containing reactive substituents at the nitrogen atoms, with the macroheterocycle (LXIII). Subsequent reduction of the tetra-amide (LXX) with diborane leads to the formation of the cylindrical macrotricyclic polythiatetra-amine (LXXI). The sulphur-containing macrotricyclic compounds (LXXII) to (LXXV) have been obtained analogously[183,184].





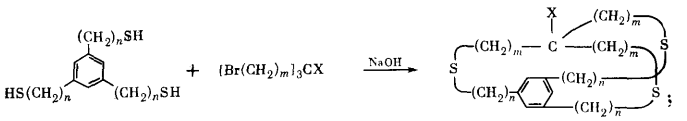


(LXIII): $n=1$, R = H;
(LXIV): $n=1$, R = Me;
(LXV): $n=1$, R = $COCH_2OCH_2COOH$;
(LXVI): $n=1$, R = $COCH_2OCH_2COOC_6H_4NO_2$-*n*;
(LXVII): $n=2$, R = Me;
(LXVIII): $n=2$, R = $COCH_2OCH_2COOH$;
(LXIX): $n=2$, R = $COCH_2OCH_2COOC_6H_4NO_2$-*n*

(LXX): $n=1$, X = O;
(LXXI): $n=1$, X = H_2;
(LXXII): $n=2$, X = O;
(LXXIII): $n=2$, X = H_2

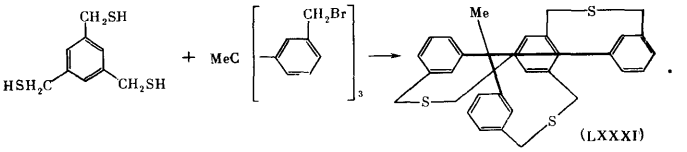
(LXXIV): X = O;
(LXXV): X = H_2

A single-stage method of synthesis of macrobicyclic sulphides[179] has been developed. The macrobicyclic compounds (LXXVI)–(LXXX) have been obtained by the reaction of 1,3,5-tris(mercaptomethyl)- or 1,3,5-tris(mercaptoethyl)-benzene with tris(bromoalkyl)methane or tris(bromoalkyl)-ethane in the presence of sodium hydroxide:



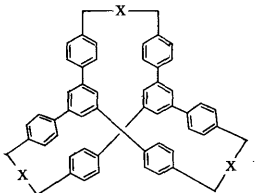
(LXXVI): $n=1$, $m=3$, X = H;
(LXXVII): $n=1$, $m=2$, X = H;
(LXXVIII): $n=2$, $m=3$, X = H;
(LXXIX): $n=2$, $m=2$, X = H;
(LXXX): $n=2$, $m=1$, X = Me.

1,3,5-Tris(mercaptomethyl)benzene has also been used to synthesise the symmetrical triply bridged [2,2,2]cyclophane (LXXXI):[180]

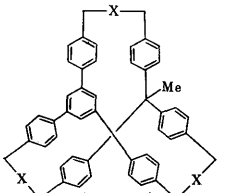


(LXXXI)

The triply bridged polythiacyclophanes (LXXXII)–(LXXXV) have also been synthesised[181]. Trithiatriphenylbenzophane has been produced by the reaction of 1,3,5-tris[(*p*-mercaptomethyl)phenyl]benzene with 1,3,5-tris[(*p*-bromomethyl)-phenyl]benzene in 31% yield:

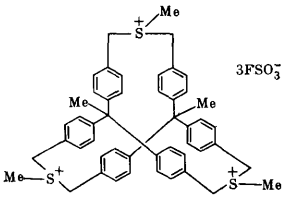


(LXXXII)
X = S, SO_2, $\overset{+}{S}Me \cdot \tilde{F}SO_3$

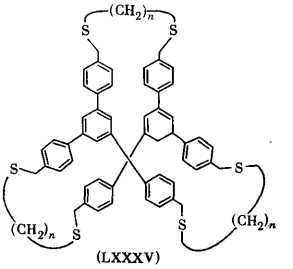


(LXXXIII)
X = SO_2, $\overset{+}{S}Me \cdot \tilde{F}SO_3$

Compounds (LXXXV) have been obtained by the reaction of 1,3,5-tris[(*p*-bromomethyl)phenyl]benzene with different α,ω-dithiols:



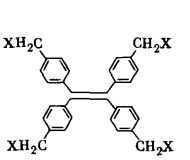
(LXXXIV)



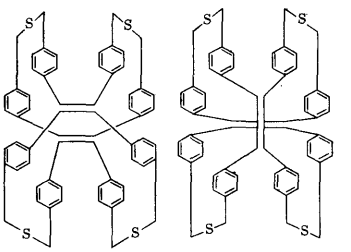
(LXXXV)
$n=2-5$

The reaction of equivalent amounts of the tetrabromo-compounds (LXXXVI) and the tetrathiol (LXXXVII) at high dilution leads to compound (LXXXVIII), with the four-sided bridged tetraphenylene system in the form of a mixture of two stereoisomers with parallel and orthogonal orientations of the central double bond (Scheme 8);[182] the yield of compound (LXXXVIII) is 4%.

Scheme 8



(LXXXVI): X = Br;
(LXXXVII): X = SH



(LXXXVIII)

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Thus analysis of the literature data has shown that the chemistry of sulphur-containing macroheterocycles has been in recent years the subject of increasing attention of investigators. This is due primarily to the possibility of using macroheterocyclic sulphides as complex-forming agents and extractants for heavy metals. New studies in this field will undoubtedly promote their wider practical application.

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