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DIBENZOTETRAAZAMACROHETEROCYCLES: SYNTHESIS AND PROPERTIES. (REVIEW)

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Data on the synthesis, complexing ability, practical applications, and biological activity of dibenzotetraazamacroheterocycles of the azacrown ether, amide, and azomethinedibenzotetraazacycloalkane types and also dibenzotetraazamacroheterocycles containing amide and azomethine fragments are classified and analyzed.

Keywords: azacrown ethers, azomethines, dibenzotetraazamacroheterocycles, macrocyclic oxamides.

At present the chemistry of nitrogen macrocycles is developing at a very high rate. Many of the compounds are highly effective extractants for metal ions [1-3], find widespread use as contrast agents for magnetic resonance imaging [4-8], and can also be used as precursors in the biosynthesis of certain types of alkaloids [9] and also as ion-selective [10] and fluorescent [11] receptors and as agents for the transport of ions through a liquid membrane in dialysis and electrodialysis [12, 13]. Chiral macrocyclic tetraamides are used as stationary phase in liquid chromatography [14]. The potentialities of nitrogen macrocycles in theoretical and practical respects have not been exhausted, and further research in the field is promising.

In the last 15 years there have been a fairly large number of monographs and reviews in which aspects of the synthesis, properties, and applications of azamacroheterocycles and their metal complexes have been touched upon [15-26]. However, there have been significantly fewer publications devoted to the various classes of dibenzotetraazamacroheterocycles (*e.g.*, dibenzotetraaza[14]annulenes [27-29], macrocyclic Schiff bases based on 2,6-diformylphenols [30]). Dibenzotetraazamacroheterocycles have found use as effective extractants for metal ions and as spectrophotometric agents [31-33], are used in the design of new magnetic materials [34], etc. To fill the gap we considered it desirable to analyze existing published material on the synthesis, complexation, and practical applications of dibenzotetraazamacrocycles of the azacrown ether, amide, azomethine, and dibenzotetraazacycloalkane types and also dibenzotetraazamacrocycles containing amide and azomethine fragments.

1. METHODS OF PRODUCTION OF MACROCYCLES

Methods for the production of certain types of tetraazamacroheterocycles are discussed below.

1.1. Dibenzotetraazacrown Ethers

Dibenzotetraazacrown ethers are obtained by the reaction of bisphenols with polyethyleneglycol ditosylates and bischloramidines and also of polyethyleneglycols containing secondary and tertiary amino

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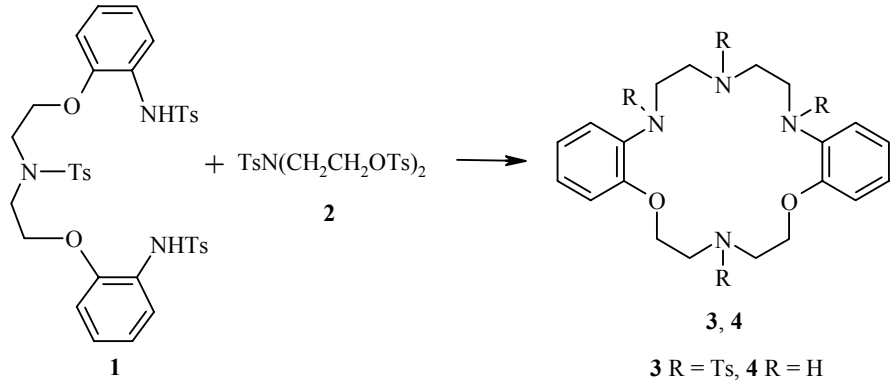
groups or benzimidazole fragments with polyethyleneglycols or amines, sometimes with the use of tosyl, trifluoroacetyl, or mesyl protection of the functional groups. Thus, the dibenzotetraazamacrocycle **3** was obtained by heating compounds **1** and **2** in DMF at 80°C for 12 h in the presence of phenoxides or sulfonylanilides and potassium carbonate as base [35].

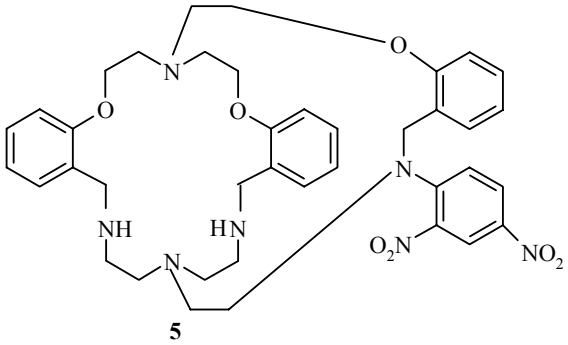


1 **3**, **4**

3 R = Ts, **4** R = H

The tosyl protection in compound **3** was removed by the action of acetic acid saturated with hydrobromic acid, resulting in the production of the corresponding N-unsubstituted macrocycle **4** with a yield of 30%.

A similar approach to the synthesis of tetraazacrown ethers (but without tosyl protection of the amino group) was used by Indian researchers [36]. The condensation of tris(2-aminoethyl)amine with tris{2-[3-(oxomethyl)phenoxy]ethyl}amine led to the formation of the unsymmetrical azacryptand **5**.



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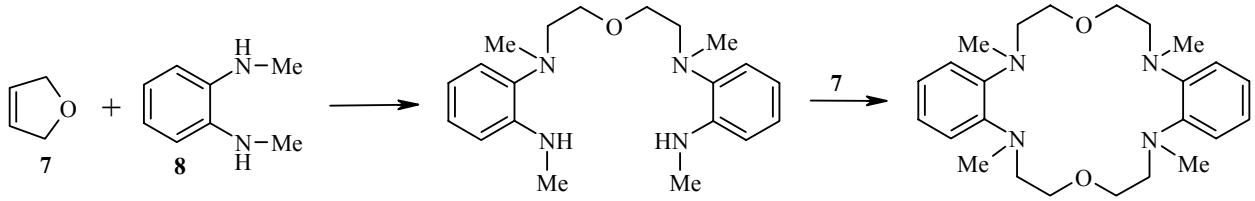
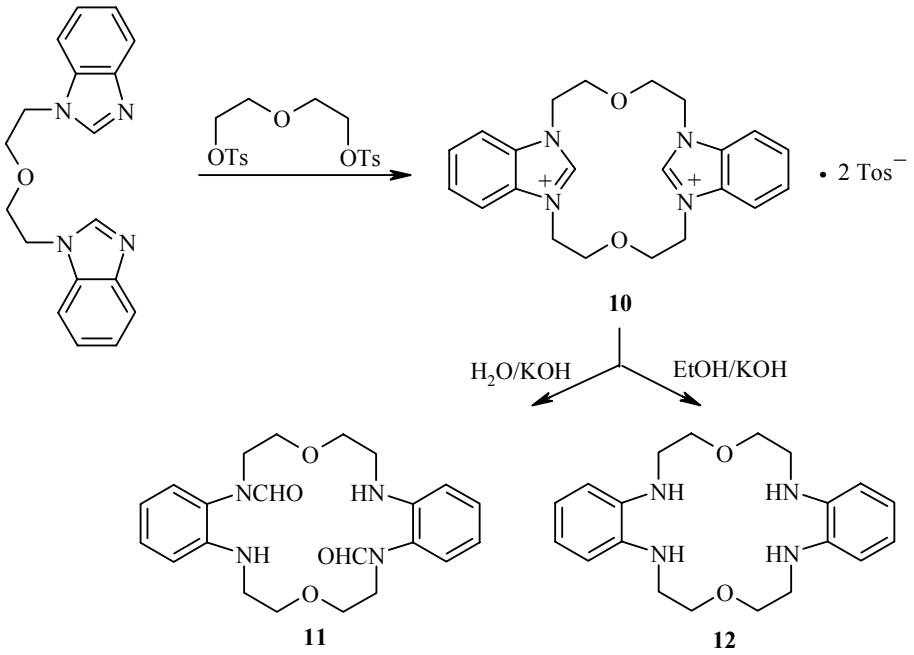
A group of Japanese authors developed a method for the synthesis of the tetraazacrown ether **6** starting from the dihydrofuran **7** and *o*-N,N'-dimethylphenylenediamine (**8**) through the intermediate **9** according to the scheme below [37].

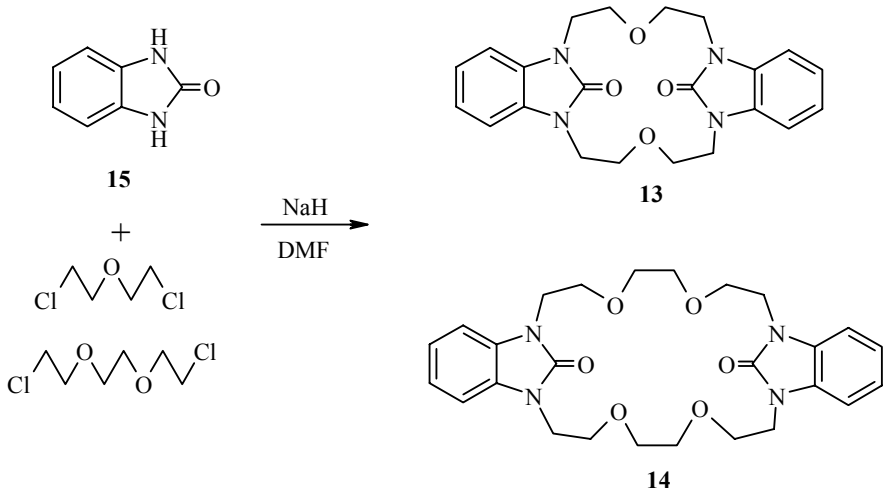


7 **8** **9** **6**

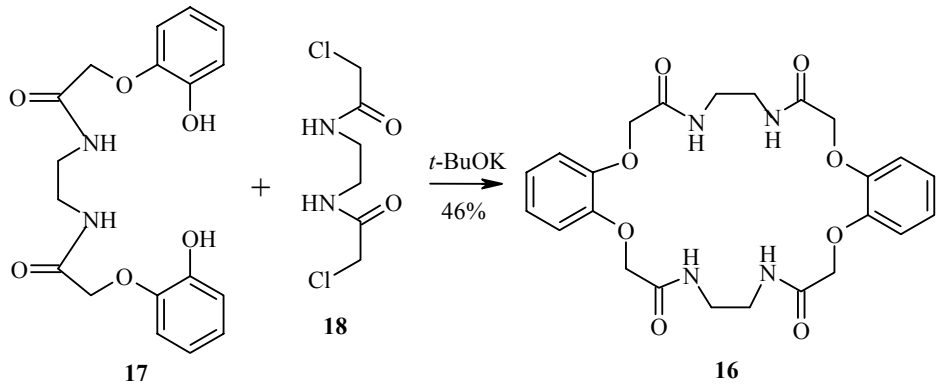
Coronands **11** and **12** of the dibenzo[18]crown-O_2N_4 type were synthesized by the cyclocondensation of $RCH_2CH_2OCH_2CH_2R$ (R = benzimidazolyl) with bis(2-tosyloxyethyl) ether followed by hydrolysis of the intermediate **10** in the presence of potassium hydroxide [38].



The production of the dibenzotetraazacrown ethers **13** and **14** by the reaction of benzimidazolone **15** with α,ω-dichloro ethers can be regarded as a modification of this method of synthesis [39].



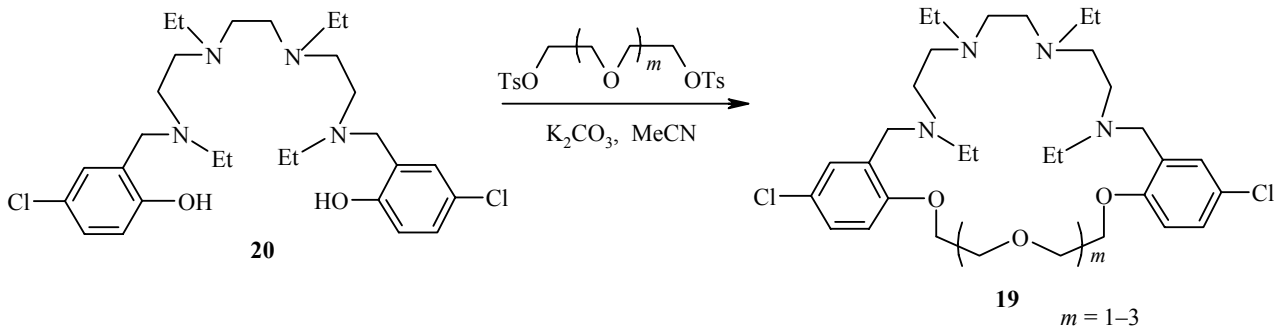
The author of [40] reported on the synthesis of dibenzotetraazacrown ethers (the tetraaza analogs of the dibenzocrown ethers containing *o*-phenylenediamine fragments) starting from benzimidazole. The macrocyclic tetraamide **16** was synthesized by the reaction of the bisphenol **17** with the "crablike" bischloramide **18** [41].



17 **18** **16**

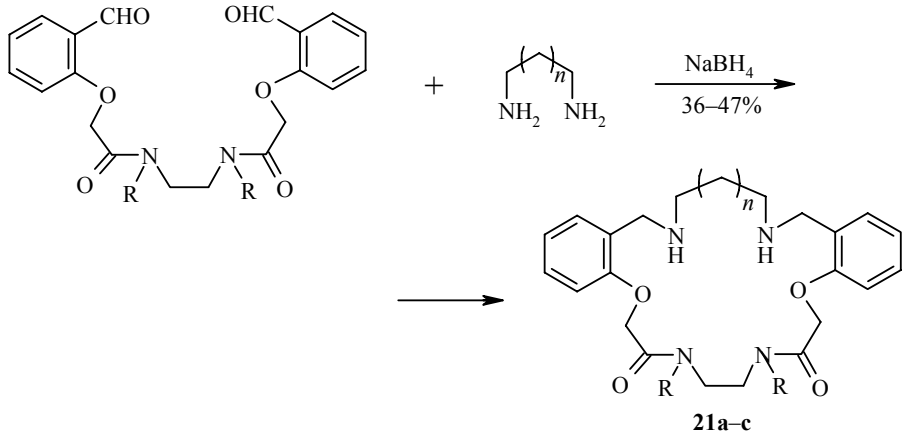
The reaction is the first example of the formation of a macrocyclic tetraamide from bis(α-chloramide) and bisphenol.

The synthesis of compounds **19** from bisphenol **20** and the ditosylates of polyethyleneglycols is known [42].



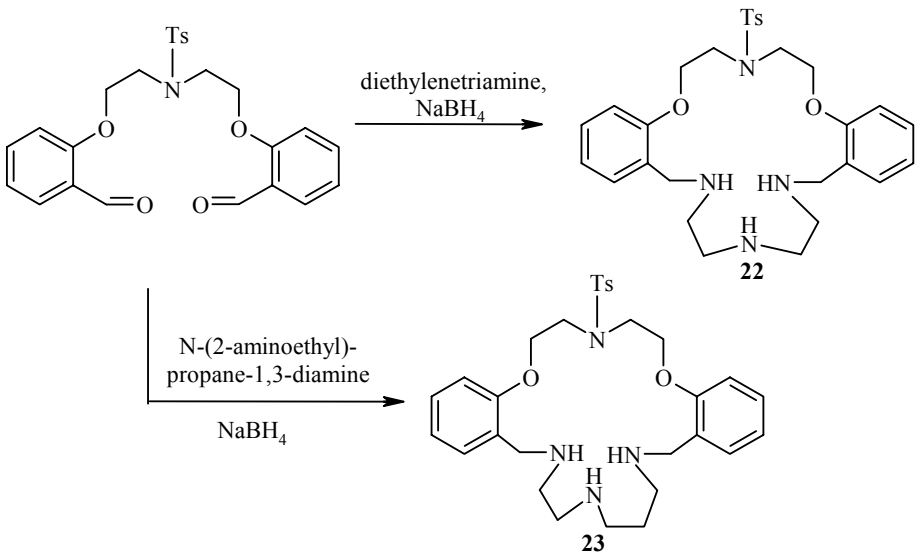
20 **19** *m* = 1–3

One of the most convenient and widely used methods for the production of dibenzotetraazacrown ethers is the reaction of dicarbonyl compounds (dialdehydes, acid dichlorides) with the corresponding diamines. Thus, this approach was used successfully by American [43] and Australian [44] investigators for the synthesis of macrocycles of types **21a-c**, **22**, and **23** respectively.



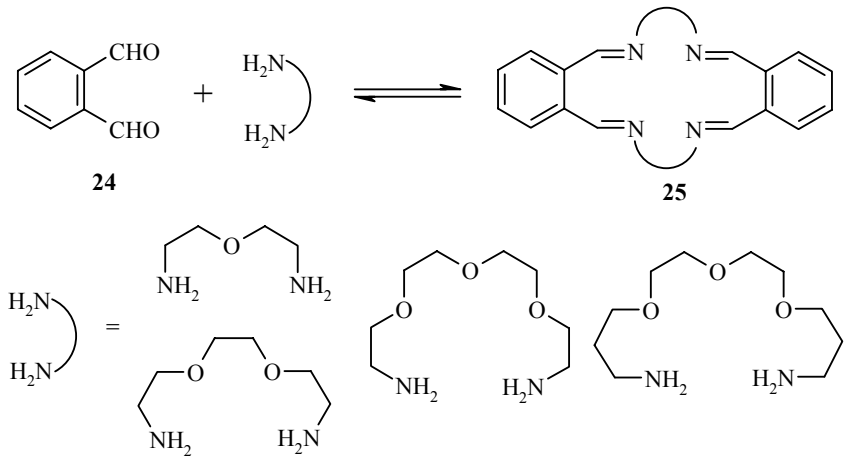
21a–c

a R = H, *n* = 1; **b** R = Me, *n* = 0; **c** R = Me, *n* = 1

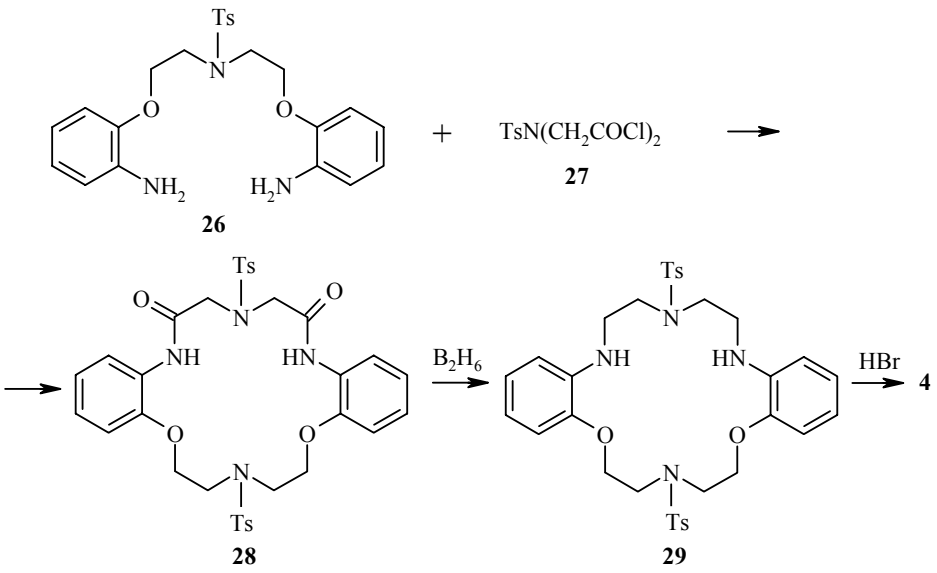


The Schiff bases were not isolated from the reaction mixture, and they were reduced *in situ* by slow addition of $NaBH_4$ to the solution.

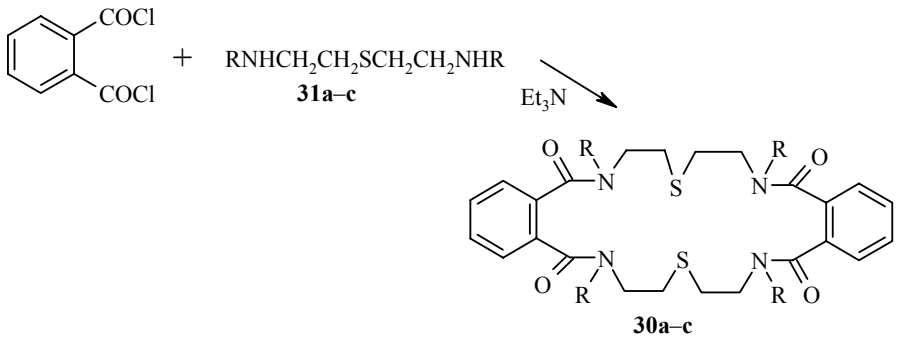
Another example of the successful realization of this approach is the use of the reversible reaction of 1,2-dialdehydes **24** with diamines in the creation of a combinatorial library of macrocycles of type **25** [45].



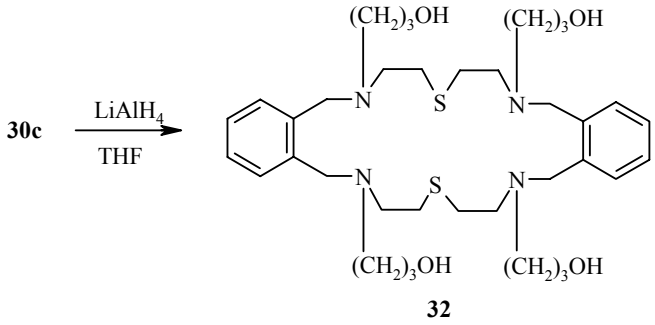
A group of Russian investigators synthesized the macrocycle **4** according to a scheme including acylation of the bridged diamine **26** with the acid dichloride **27** under conditions of high dilution. The macrocyclic diamide **28** formed here was reduced with B_2H_6 to the corresponding diamine **29**, from which the macrocycle **4** was formed after removal of the protecting groups [46].



A series of dibenzotetraazadithiacrown ethers **30a-c** were synthesized in a similar way [47]. However, it should be noted that in the last case cyclocondensation of the diamines **31a-c** with phthaloyl chloride takes place by a mechanism of the [2+2] type.



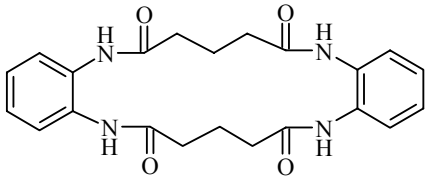
a R = H, **b** R = CH_2CH_2Ph, **c** R = CH_2CH_2COOMe



Reduction of the macrocycle **30c** by the action of lithium aluminum hydride leads to the macrocycle **32** with a yield of up to 80%. Further modification of the exocyclic functional groups for compound **30c** was examined in [48].

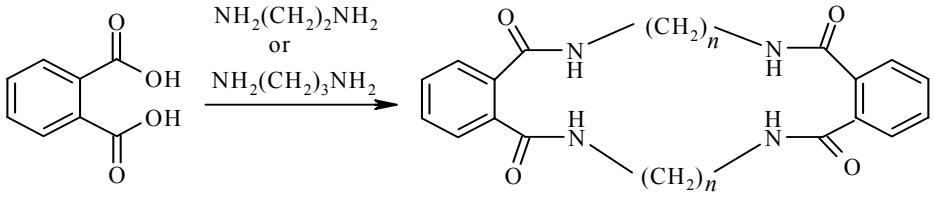
1.2. Dibenzotetraazamacroheterocycles Containing Amide Fragments

As in the case of dibenzotetraazacrown ethers, the most general method for the production of amide dibenzotetraazamacroheterocycles is the reaction of diamines with dicarbonyl compounds [dialdehydes (for the synthesis of macrocycles of type **21a-c**), dicarboxylic acids, the dichlorides of dicarboxylic acids (for the synthesis of compounds **28** and **30a-c**), the diesters of dicarboxylic acids]. Thus, the template condensation of glutaric acid with *o*-phenylenediamine gave the Sn(II) complex of the macrocycle **33** [49].



33

The reaction of phthalic acid with ethylenediamine or 1,3-diaminopropane in the presence of condensing agents (dicyclohexylcarbodiimide, 4-dimethylaminopyridine) leads to the formation of a series of 16- and 18-membered macrocycles **34a**,**b** [50].

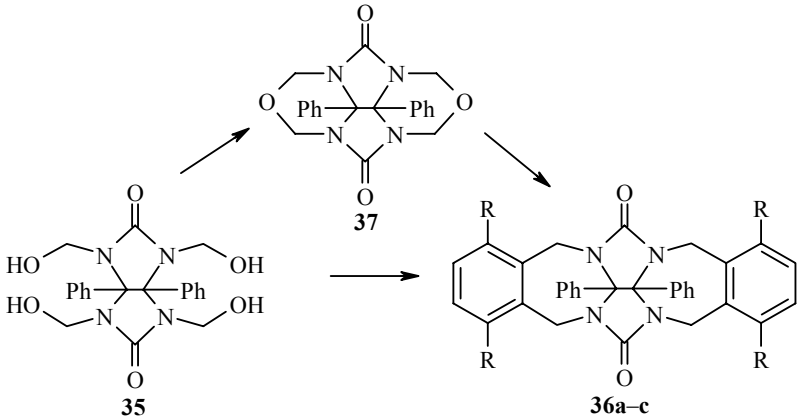


34a,**b**

a n = 2, **b** n = 3

Earlier [51] the synthesis of compound **34b** from dimethyl phthalate and 1,3-diaminopropane was described.

A different approach to the synthesis of amide dibenzotetraazamacroheterocycles was demonstrated in [52]. The reaction of tetrakis(hydroxymethyl)diphenylglycoluril **35** with various aromatic substrates (benzene, hydroquinone, 1,4-dimethoxybenzene) in an acidic medium gave compounds **36a**,**c**. The cyclic ether **37** is clearly an intermediate in this reaction. The reaction can also be used for the production of compounds **36a-c**.



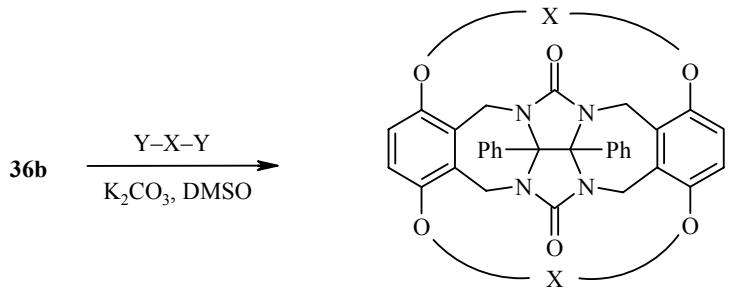
37

35

36a–c

36 **a** R = H, **b** R = OH, **c** R = OMe

The structure of compound **36b** was confirmed by data from X-ray crystallographic analysis [53]. Compounds **38a-e**, containing ether side chains, were synthesized on the basis of the macrocycle **36b** [52, 54].

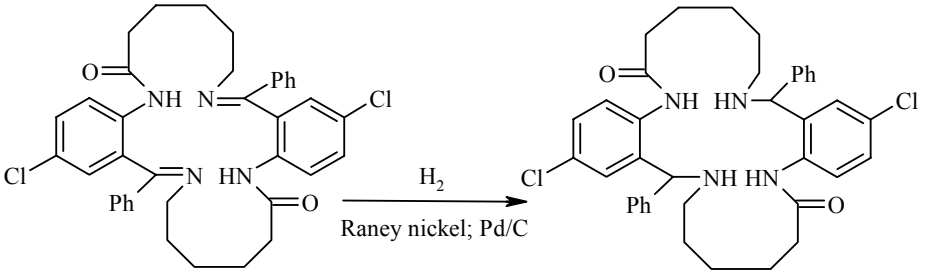


38a–e

Y = Cl, Br; **a** X = $–(CH_2)_6–$, **b** X = $–(CH_2CH_2O)_2CH_2CH_2–$,
c X = $–(CH_2CH_2O)_3CH_2CH_2–$; **d** X = $–(CH_2CH_2O)_4CH_2CH_2–$,
e X = $CH_2CH_2OCH_2CH_2NRCH_2CH_2OCH_2CH_2$

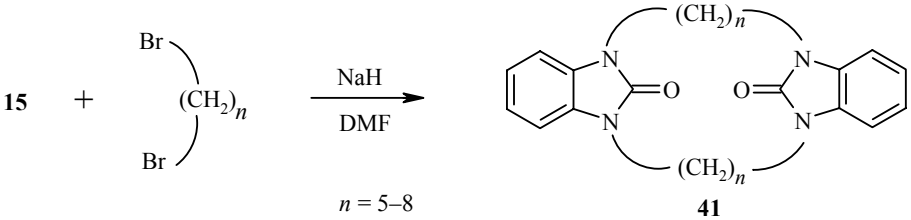
In [55] it was proposed to use benzocrown ethers as aromatic substrate for the production of structures of the **36a-c** type, while in [56, 57] the use of dipyridineglycoluril and ditoluoylglycoluril was described. The synthesis of tetrapodands based on diphenylglycoluril was described in [58].

Another method for the production of amides of dibenzotetraazamacrocycles is reduction of the azomethine bond in dibenzotetraazamacroheterocycles containing amide and azomethine fragments. Thus, the macrocycle **39** can be obtained by hydrogenation of the macrocycle **40** with hydrogen over Raney nickel or in the presence of palladium on charcoal [59].



40 **39**

The production of amide dibenzotetraazacrown ethers **13** and **14** by the reaction of benzimidazolone **15** with α,ω-dichloro ethers [39] was described above. The macrocycles **41** are produced similarly from compound **15** and α,ω-dibromoalkanes.

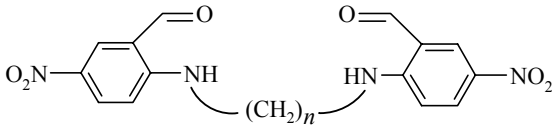


41

1.3. Macrocyclic Azomethines

Among the variety of methods for the production of this type of macrocycle it is possible to single out the two most important: The condensation of dicarbonyl compounds with diamines and the reaction of diamines with dihalides. In both cases the reaction can be carried out both with and without the use of template metal ions.

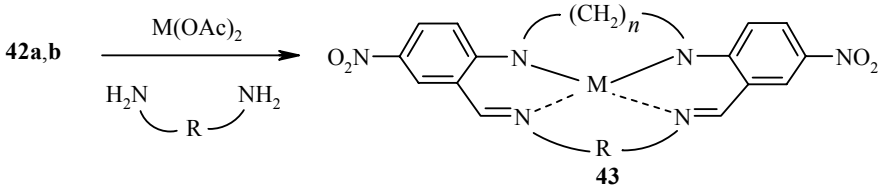
It is known [60, 61] that among the derivatives of *o*-aminocarbonyl compounds some of the most suitable ligands for template construction of the macrocycles are the diaminodialdehydes **42a**,**b**.



42a,**b**

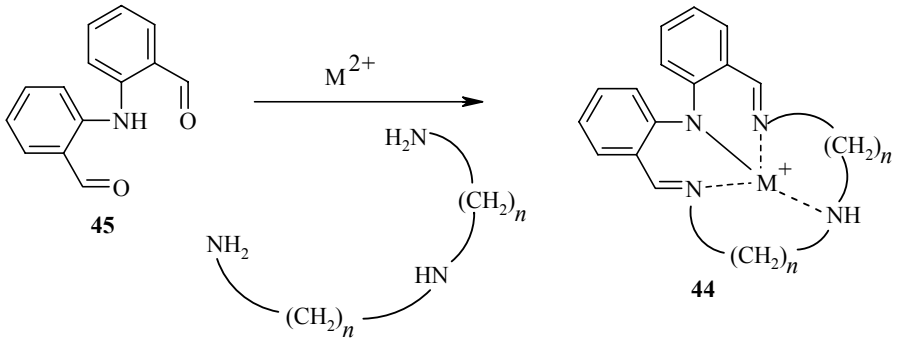
a $n = 2$, **b** $n = 3$

The latter react with diamines $H_2N–R–NH_2$ on divalent nickel, cobalt, and copper matrices with the formation of the respective complexes with macrocyclic ligands **43**.



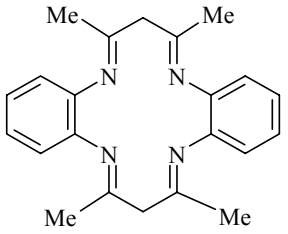
43 $n = 2, 3$; R = $–(CH_2)_2–$; $–(CH_2)_3–$; $–CH_2CMe_2–$; M = Ni, Co, Cu

A similar approach was used in [62, 63] to prepare metal complexes of dibenzocorromins. The production of metal complexes of the macrocycles **4**) by template synthesis from 2,2'-iminobisbenzaldehyde (**45**) and the respective amines is known [64, 65].



M = Ni, Co, Cu; $n = 2, 3$

The condensation of *o*-phenylenediamine with bis(acetylacetone)ethylenediimine in the presence of metal salts gave the corresponding complexes $M(L)Cl_2$ [M = Fe, Co, Cu, Ni, L = **46**], $[M(L)SO_4 \cdot H_2O]$ (M = Fe, Co), $[NiL]SO_4$, and $[CuL(SO_4)_2]$ [66].



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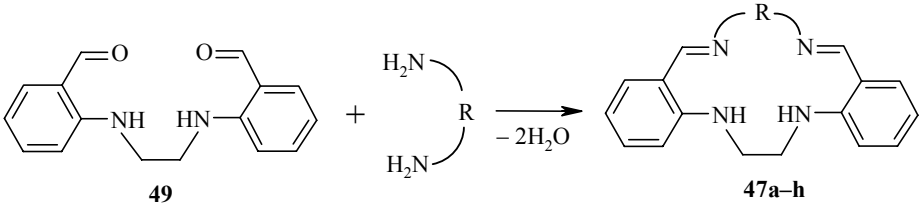
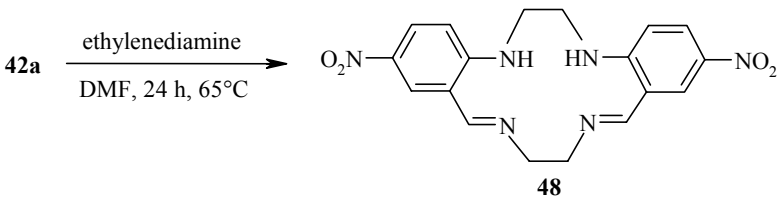
A nontemplate synthesis of the macrocyclic azomethines **47a-h** and **48** from dibenzo-containing dialdehydes **49** and **42a** and the respective diamines was described in [67, 68].



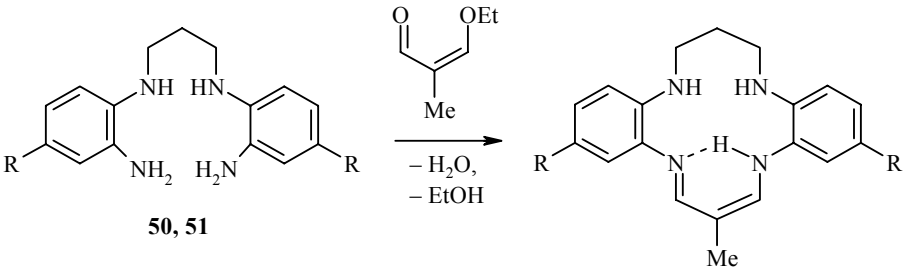
49 **47a–h**

a R = –$(CH_2)_2$, **b** R = –$(CH_2)_3$, **c** R = –$(CH_2)_4$–, **d** R = –$(CH_2)_5$–, **e** R = –$(CH_2)_7$–, **f** R = –$(CH_2)_8$–, **g** R = $(CH_2)_{10}$–, **h** R = –C(CN)=C(CN)–



48

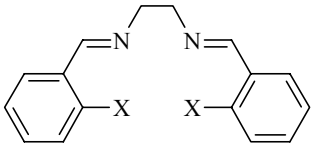
A similar approach was proposed by the authors of [69]. Compounds **52** and **53** were produced by the reaction of open-chain tetraamines of [1,3-bis(*o*-aminophenylamino)propane (**50**) or 1,3-bis(*o*-amino-*p*-methylphenylamino)propane (**51**) with 3-ethoxy-2-methylacrolein without using the high dilution technique.



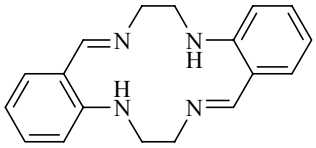
50, 51 **52, 53**

50, 52 R = H, **51, 53** R = Me

As already mentioned above, another suitable method for the production of dibenzotetraazamacroheterocycles containing an azomethine fragment is the reaction of diamines with dihalides. Thus, the 14-membered macrocycle **55** is formed when compound **54a** is boiled in ethylenediamine. It was noticed that compound **54b** is inert toward boiling ethylenediamine, but the use of copper powder as catalyst made it possible to convert compound **54b** quickly and with high yield into **55**. The 16-membered macrocycle **56** was obtained similarly from 1,3-diaminopropane [70].



54a,**b**
a X = F, **b** X = Cl



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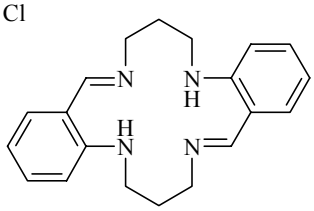
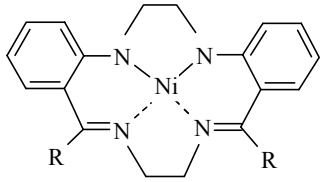


56

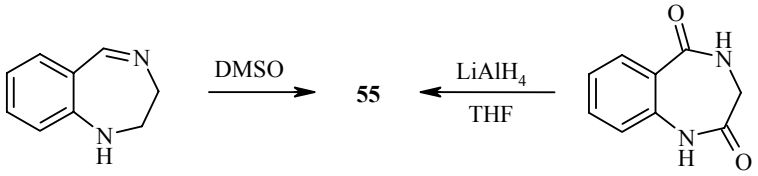
A template version of this method of synthesis was described in [71]. The condensation of nickel complexes of the Schiff bases obtained from ethylenediamine and *o*-amino aryl ketones with ethylene dibromide gave the nickel complexes of macrocycles **57a-c**.



57a–**c**
a R = H, **b** R = Me, **c** R = Ph

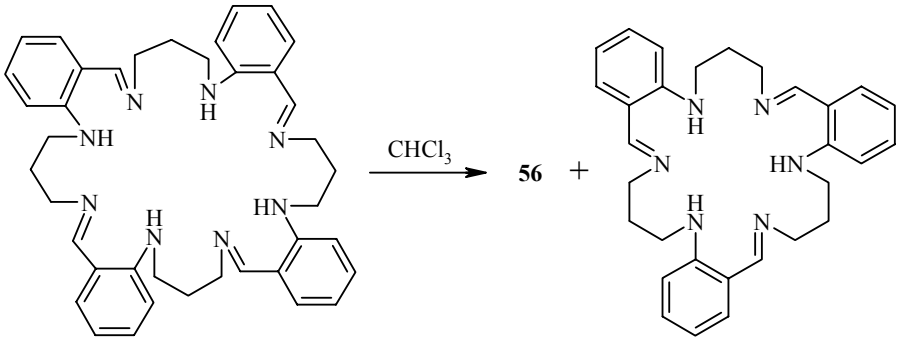
In conclusion it would be desirable to point out a few other methods for the synthesis of iminodibenzotetraazamacroheterocycles that have not received widespread use (rearrangement with ring opening and subsequent recyclization, oxidation of aminodibenzotetraazamacroheterocycles, and certain other methods).

Thus, in the previously mentioned paper [70] the slow transformation of 2,3-dihydro-1,4-benzodiazepine (**58**) to the macrocycle **55** when it was dissolved in DMSO was reported. Compound **55** can also be obtained by reduction of the diazepinedione **59** with lithium aluminum hydride in THF.



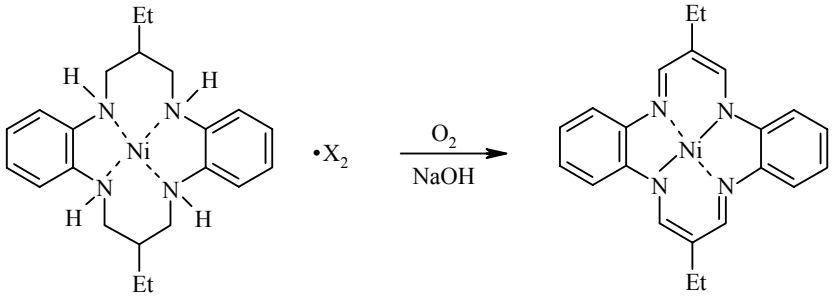
58 **59**

According to the data from some authors [72], propylene-1,3-diamine and 2-chlorobenzaldehyde enter into the reaction in the presence of copper and HCO_2H, giving the 32-membered octaazatetraimine **60** with a yield of 26%. In chloroform compound **60** rearranges to an equilibrium mixture of the previously mentioned 16-membered tetraazadiimine **56** and the 24-membered hexaazatriimine **61**.



60 **61**

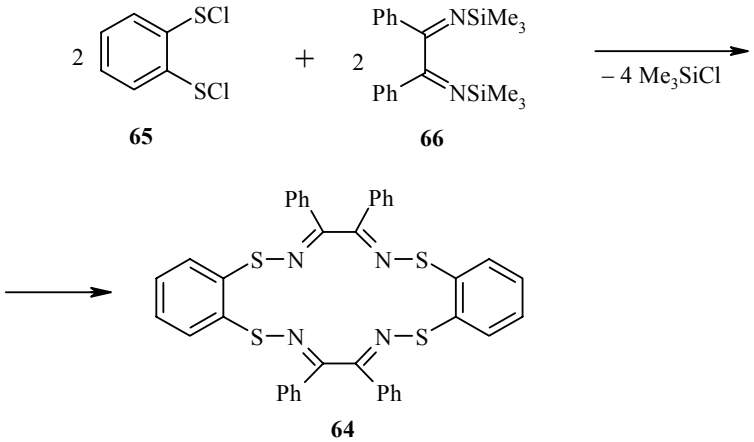
Methanol solutions of the nickel complexes of the two isomers of the tetraazamacrocycle **62a**,**b** are oxidized by atmospheric oxygen and are transformed in an alkaline medium into the nickel complex **63** [73].



62a,**b** **63**

X = ClO_4, Cl

The macrocycle **64** was synthesized with a yield of 75% by the [2+2] cyclocondensation of the two bifunctional reagents 1,2-bis(chlorothio)benzene (**65**) and benzylbis(trimethylsilyl)imine (**66**) in methylene chloride [74]. X-ray crystallographic analysis was carried out for the macrocycle **64**.

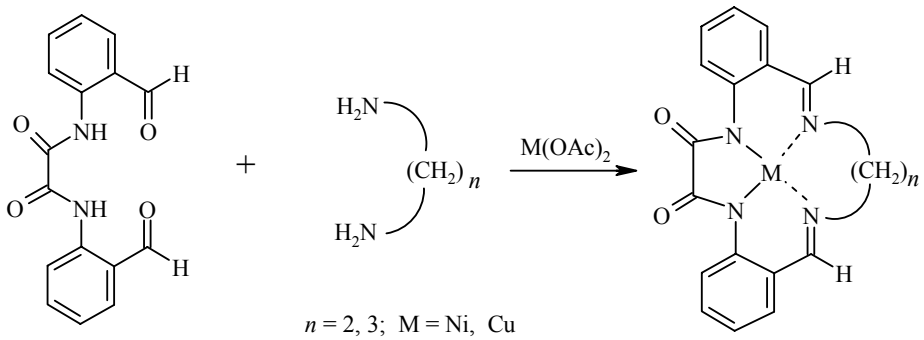


65 **66**

64

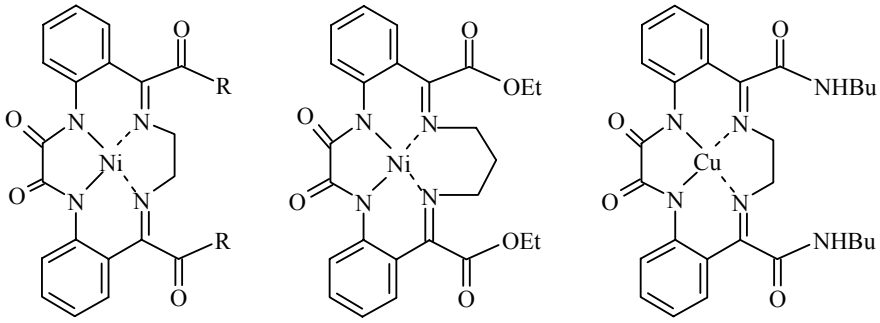
1.4. Dibenzotetraazamacroheterocycles Containing Amide and Azomethine Fragments

The main method for the synthesis of macrocycles containing amide and azomethine fragments is [1+1] template condensation of dicarbonyl compounds (dialdehydes, diamides, bis-α-ketoesters) with diamines. Thus, the complexes of macrocycles **68** were obtained by the reaction of the diformyloxanilide **67** with ethylenediamine and 1,3-diaminopropane on Ni^{2+} and Cu^{2+} matrices [75].

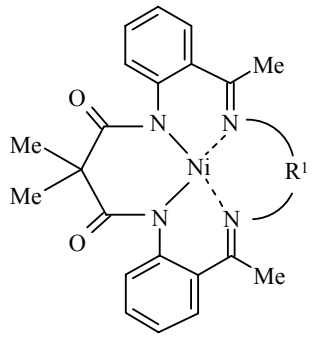


67 **68**

The complexes of macrocycles **69-72** were obtained similarly [76-78].



69 **70** **71**

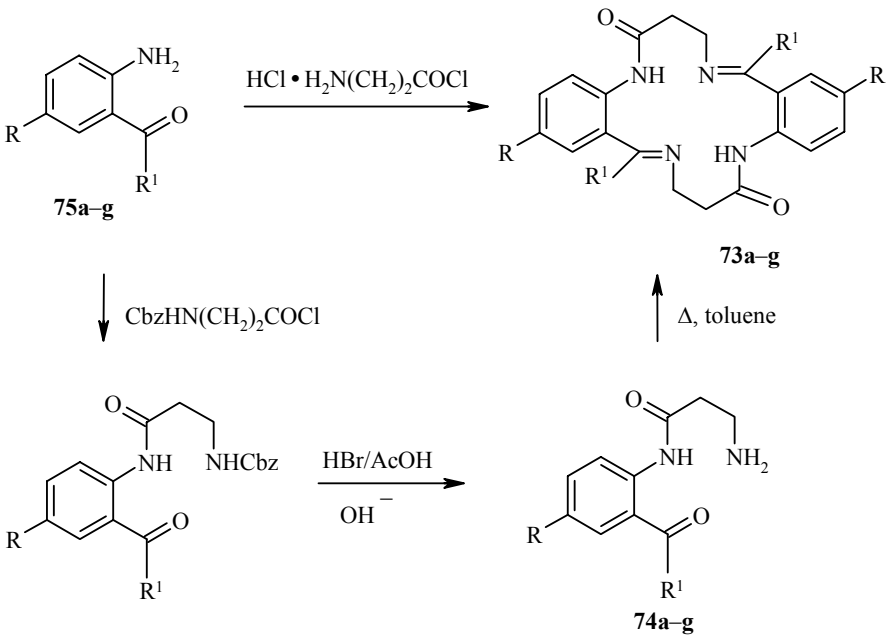


72

69 R = OMe, OEt, $OCHMe_2$, $OCMe_3$, NH_2, NHBu, $NH(CH_2)_3Me$, NHPh, *n*-$HNC_6H_4NMe_2$, *n*-$HNC_6H_4NO_2$, NMe_2, pyrrolidin-1-yl, morpholin-4-yl;

72 R^1 = CH_2CHMe, $CH_2CH_2CH_2$

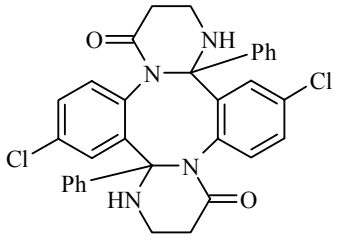
The synthesis of the macrocycles **73a-g** by cyclocondensation of the amides of amino acids **74a-g** by boiling in toluene [79, 80] can be regarded as a modification of the above-mentioned method of synthesis.



75a–g **73a–g** **74a–g**

a R = H, R^1 = Ph; **b** R = Cl, R^1 = Ph; **c** R = Br, R^1 = Ph; **d** R = Me, R^1 = Ph; **e** R = Br, R^1 = *o*-BrC_6H_4; **f** R = Br, R^1 = *p*-ClC_6H_4; **g** R = NO_2, R^1 = Ph; Cbz = –$COOCH_2Ph$

An alternative method for the synthesis of the macrocycles **73a-g** is the condensation of 5-substituted 2-aminobenzophenones **75a-g** with the hydrochloride of β-alanyl chloride by boiling in chloroform. The question of the structure of the macrocycle **73b** was not resolved conclusively in [79] in so far as an alternative structure **76** was used for it. The structure of compounds **73a**,**f** was confirmed by X-ray crystallographic analysis [81, 82] (Fig. 1, for compound **73f**).



76

The production of the 1,9-dimethyl derivatives of macroheterocycles **73b-d**,**f**,**g** was described in [83].

A series of 22-membered dibenzotetraazamacroheterocycles **78a-h**, **40** were synthesized by the cyclocondensation of 5-substituted 2-(ε-aminocaproyl)amidobenzophenones **77a-i** under conditions similar to those described above [84, 85]. The methylation of compounds **78a** and **40** was described in [59]. The mass spectra of the macrocycles **78a-c** and **40** were obtained [86].

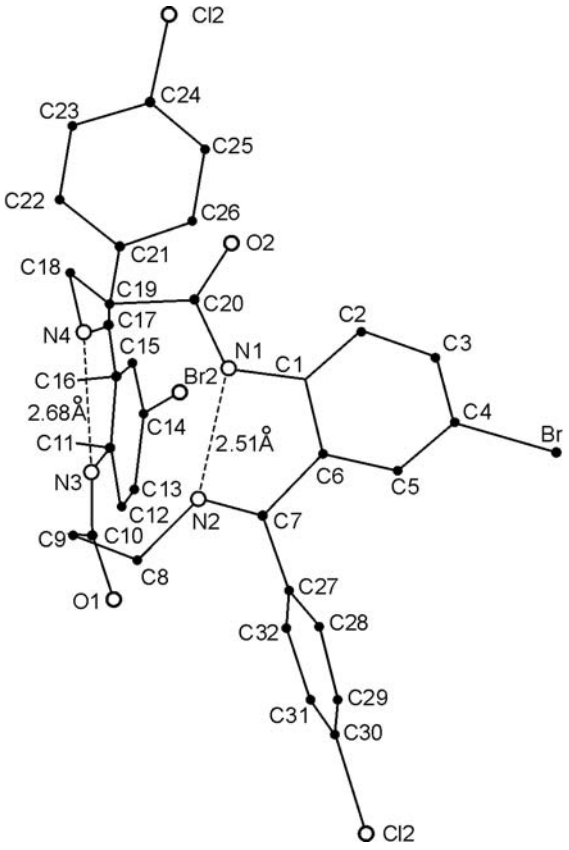
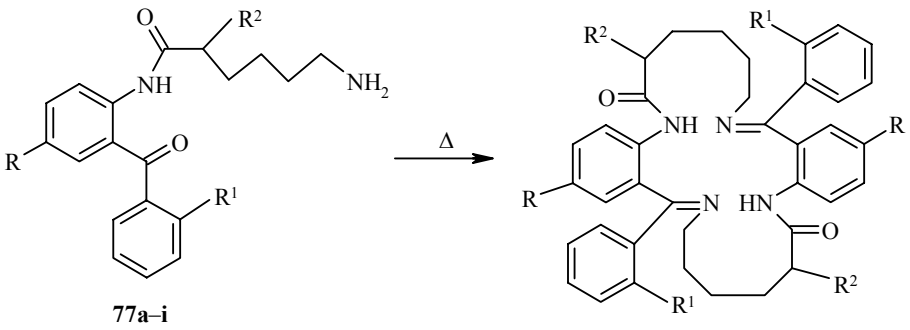


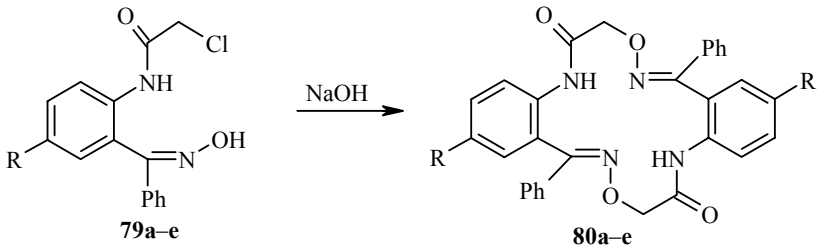
Fig. 1. The structure of compound **73f**.



77a–i **78a–h**, **40**

77, **78 a** R = Br, $R^1 = R^2 = H$; **b** R = NO_2, $R^1 = R^2 = H$; **c** R = Me, $R^1 = R^2 = H$;
d R = Me, $R^1 = H$, R^2 = NHTs; **e** R = Cl, $R^1 = H$, R^2 = NHTs; **f** R = Br, $R^1 = H$, R^2 = NHTs;
g R = Br, R^1 = Cl, R^2 = NHTs; **h** R = NO_2, $R^1 = H$, R^2 = NHTs; **77 i, 40** R = Cl, $R^1 = R^2 = H$

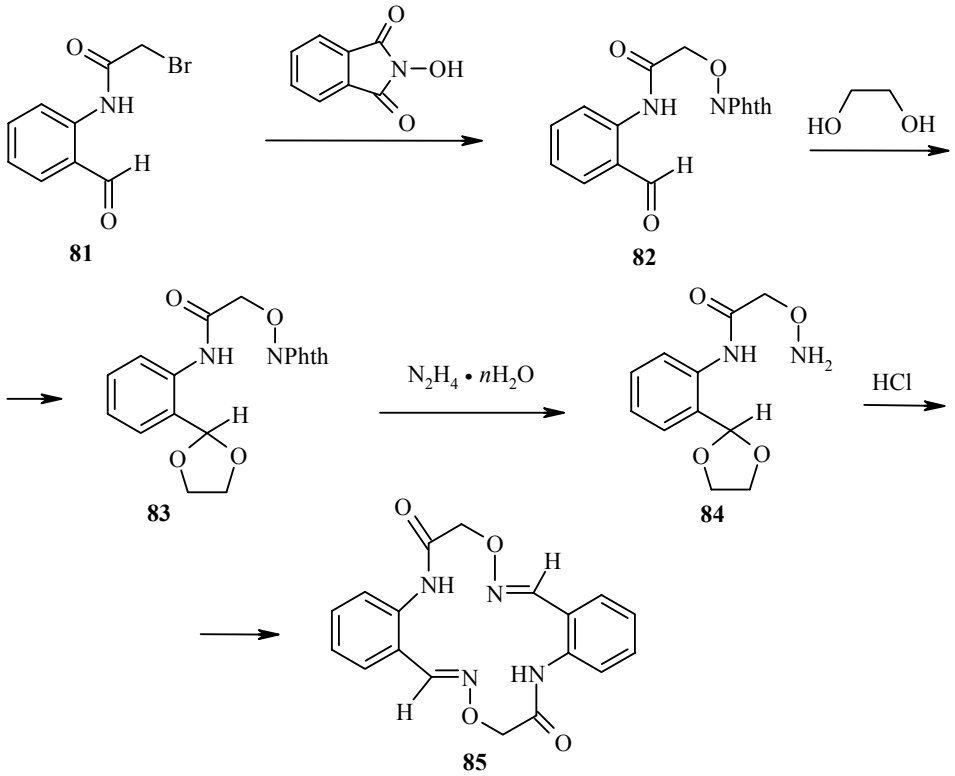
Another important method for the synthesis of macrocycles containing amide and azomethine bonds is O-alkylation of the *syn* isomers of 5-substituted 2-chloroacetamidobenzophenone oximes **79a-e** [87, 88].



79a–e **80a–e**

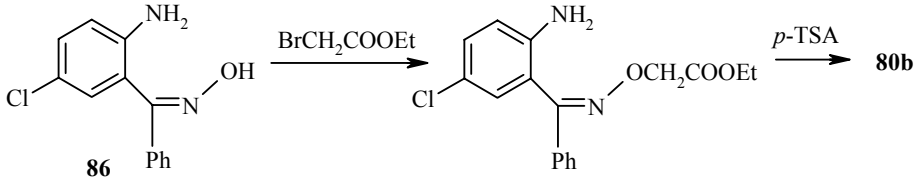
a R = H, **b** R = Cl, **c** R = Br, **d** R = Me, **e** R = NO_2

An alternative method for the synthesis of macroheterocycles of type **80a-e** is the scheme proposed in [89]. The reaction of 2-bromo-2'-formylacetanilide (**81**) with N-hydroxyphthalimide gave the respective N-hydroxyphthalimide derivative **82**, treatment of which with ethylene glycol in the presence of *p*-toluenesulfonic acid led to the formation of 2'-(1,3-dioxan-2-yl)-2-phthalimidoacetanilide (**83**). During hydrazinolysis the latter was converted into 2-aminoxy-2'-(1,3-dioxan-2-yl)acetanilide (**84**), the cyclization of which in the presence of HCl gave the 16-membered macrocycle **85**.



81 **82** **83** **84** **85**

Macrocycles of type **80a-e** can also be obtained according to the scheme described in [87]. In order to obtain evidence for the structure of the obtained macrocycle **80b** it was synthesized from the *syn* isomer of 2-amino-5-chlorobenzophenone oxime **86**.



86

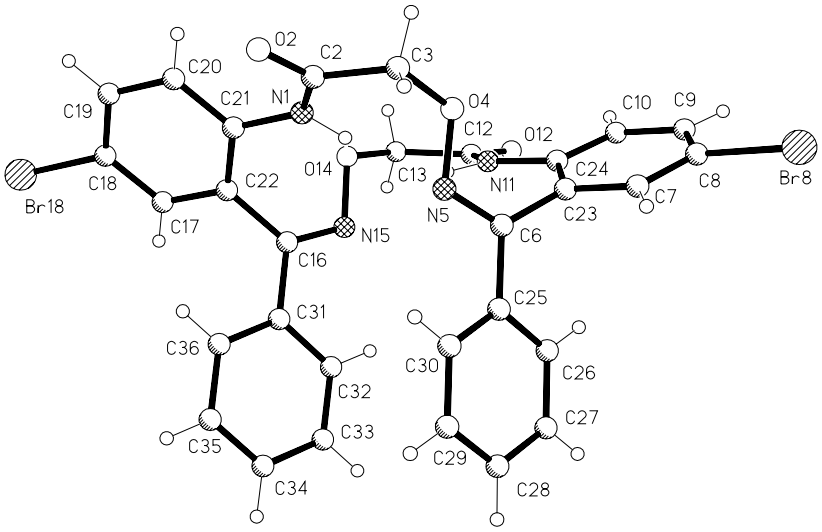
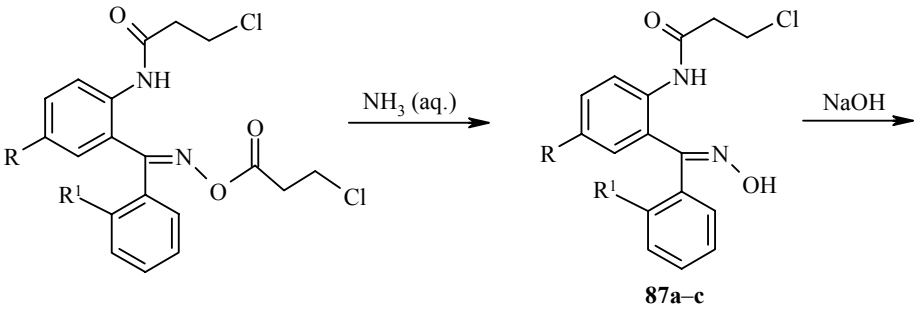


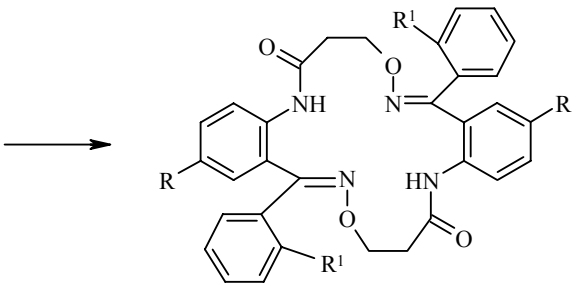
Fig. 2. The structure of compound **80c**.

We described the chemical properties of the heterocycles **80c**,**d** in [90] and the crystal and molecular structures of the inclusion compound of the macrocycle **80c** with benzene in [91] (Fig. 2).

We established that treatment of the *anti* isomers of the oximes of 5-substituted 2-(β-chloropropionylamino)benzophenones **87a-c** with an equimolar amount of sodium hydroxide led to the formation of 18-membered macrocycles **88a-c** [92, 93].



87a–c



88a–c

a R = Me, R^1 = H; **b** R = Br, R^1 = H; **c** R = Br, R^1 = Cl

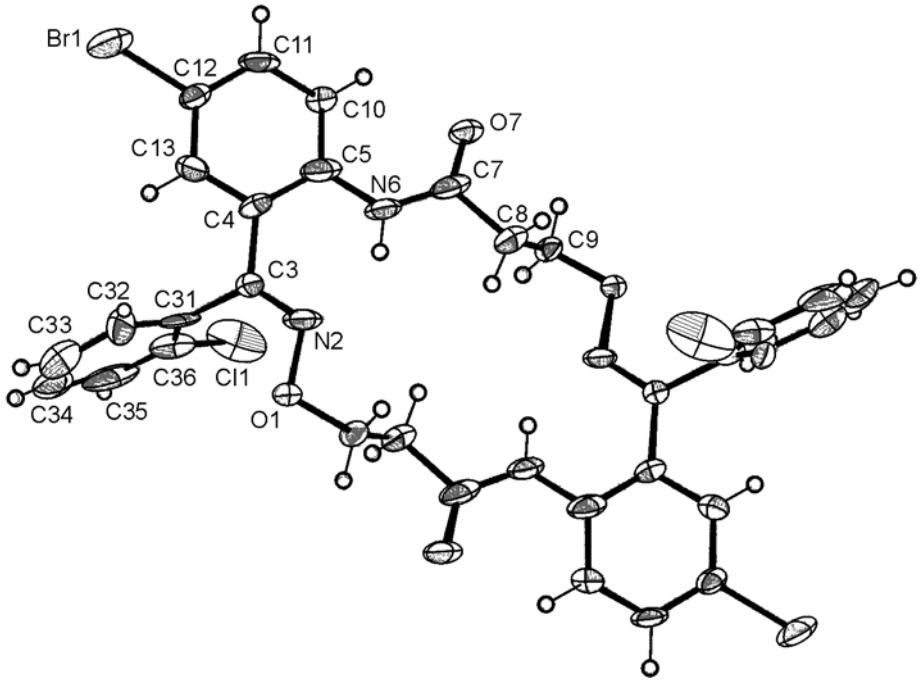
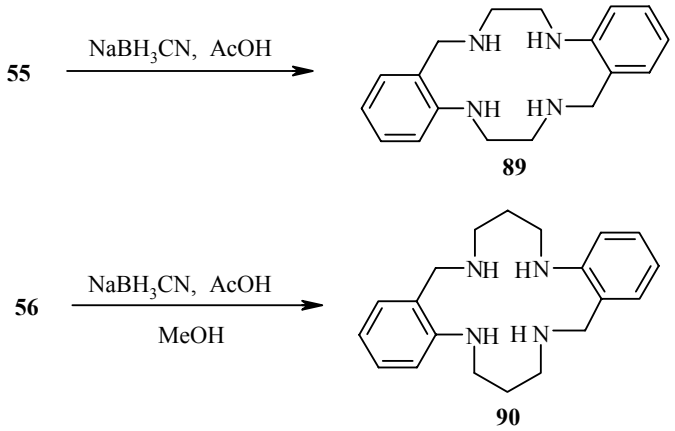


Fig. 3. The structure of compound **88c**.

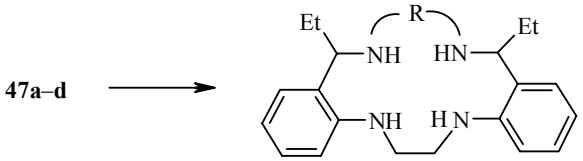
A comparative study of the fragmentation of 16- and 18-membered dibenzotetraazamacroheterocycles of the **80a-e** and **88a-c** type under electron impact was undertaken [94]. The structure of one representative of the series of 18-membered macroheterocycles **88c** was confirmed by X-ray crystallographic analysis (Fig. 3) [95].

1.5. Dibenzotetraazacycloalkanes

Two groups of methods have mainly been used for the synthesis of dibenzotetraazacycloalkanes, *i.e.*, reduction of the corresponding imino- and amidodibenzotetraazamacroheterocycles and the reaction of diamines with ligands. Thus, the reduction of compound **55** [70] gave the macrocycle **89**, whereas reduction of its 16-membered analog **56** led to the formation of the cyclic tetraamine **90** [72].



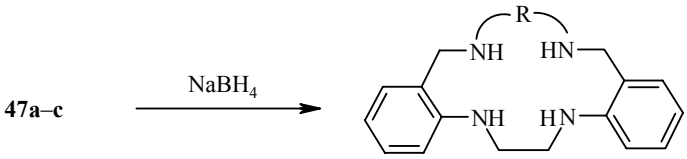
The stereoselective C-alkylation of diimine macrocycles was described in [96]. It was shown that diimines of type **47a-d**, the synthesis of which was described in [68], can form neutral magnesium complexes in reaction with two moles of EtMgBr. The use of an excess of the Grignard reagent leads to C-alkylation of the imine groups, which makes it possible to obtain after hydrolysis the diethyl-substituted tetraamines **91a-d**.



91a–d (87–94%)

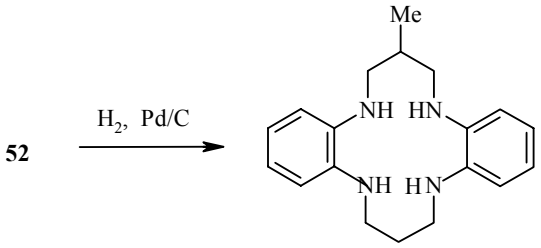
a R = $-(CH_2)_2-$, **b** R = $-(CH_2)_3-$, **c** R = $-(CH_2)_4-$, **d** R = $-(CH_2)_5-$

The synthesis of macrocyclic tetramines **92a-c** and **93** by reduction of the respective diimine precursors **47a-c** and **52** was also described [97].



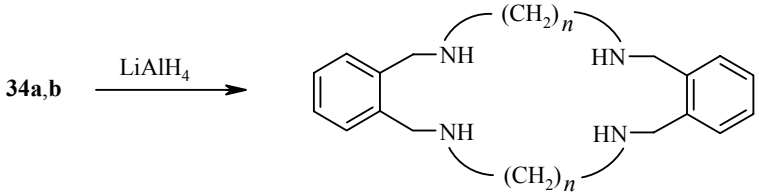
92a–c

a R = $-(CH_2)_2-$, **b** R = $-(CH_2)_3-$, **c** R = $-(CH_2)_4-$



93

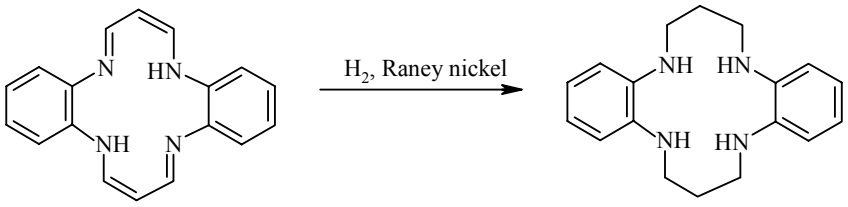
The macrocycles **94a**,**b** were obtained by the reduction of compounds **34a**,**b** with lithium aluminum hydride [50].



94a,**b**

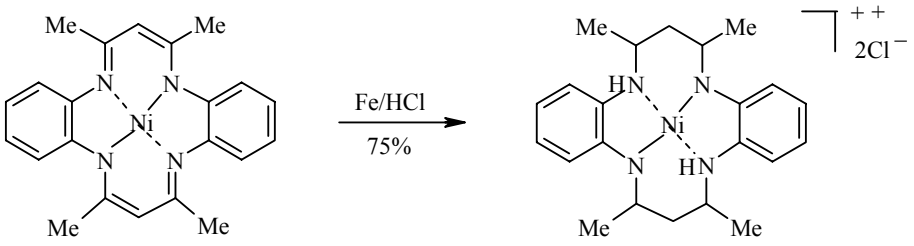
a n = 2, **b** n = 3

The dibenzomacrocycle **96** was obtained with yields of 34 [98] and 74% [99] by the hydrogenation of dibenzotetraaza[14]annulene **95** with hydrogen over Raney nickel.



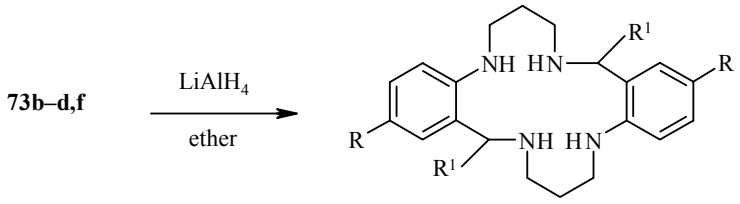
95 **96**

The synthesis of the N',N'',N''',N''''-tetramethyl derivative of compound **96** was described in [100]. The compound $[Ni(Me_4Bzo_2[14]aneN_4)]Cl_2$ (**98**) was synthesized by the reduction of the nickel complex $[Ni(Me_4Bzo_2taa)]$ (**97**) [101].



97 **98**

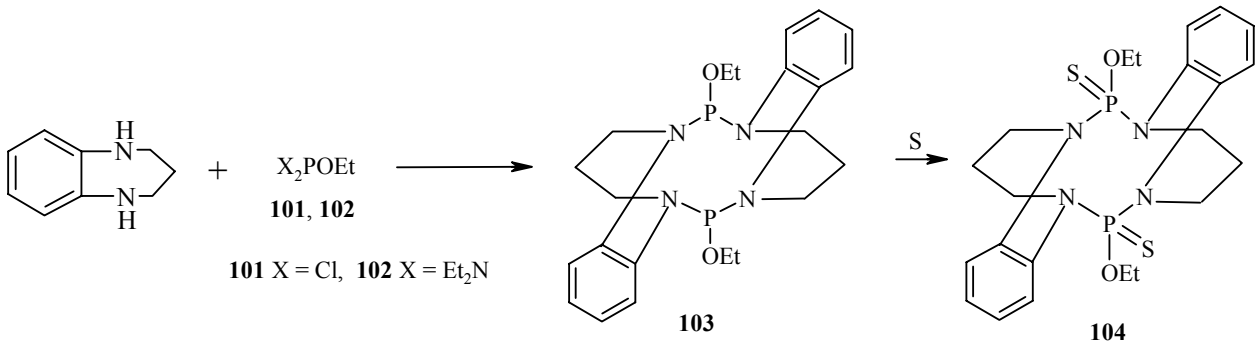
The macrocycles **99** were obtained by the reduction of compounds **73b-d**,**f** [83].



99

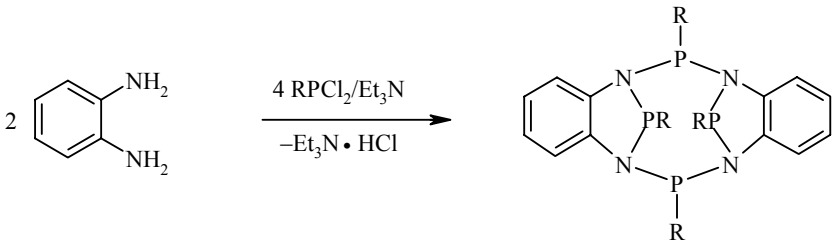
R = Cl, Br, Me; R^1 = Ph, *p*-ClC_6H_4

Phosphorylation of 2,3-benzo-1,4-diazacycloheptane (**100**) with the acid dichloride **101** or the tetraethyldiamide **102** of ethylphosphorous acid led to the formation of the dimeric compound **103**. Sulfurization of this dimer takes place under mild conditions at 40-50°C in benzene solution and leads to the formation of the macrocycle **104** [102].



103 **104**

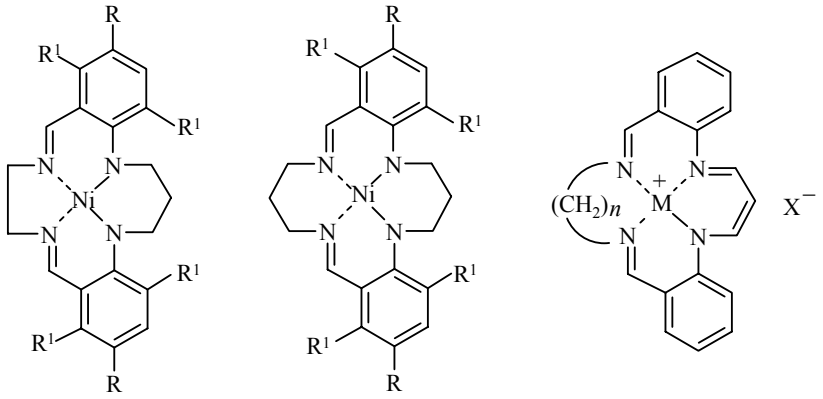
The macrocycle **105** was obtained by the reaction of *o*-diphenylenediamine with $RPCl_2$ (R = Me, Ph) in the presence of triethylamine [103].



R = Me, Ph **105**

2. COMPLEXING ABILITY AND POSSIBLE PRACTICAL APPLICATIONS OF DIBENZOTETRAAZAMACROHETEROCYCLES

The complexes of dibenzotetraazamacroheterocycles can be produced both directly in the course of synthesis (the template method) and by the reaction of the ligand with the salts of various metals in solution. Thus, the template method was used for the production of the complexes of macrocycles **43**, **44**, **46**, **57a-c**, and **68-72** and also complexes of types **106a-g**, **107a-g**, and **108** [62, 63].



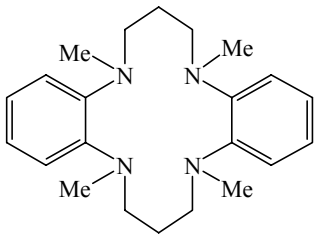
106a–g **107a–g** **108**

106, **107 a** R = R^1 = H; **b** R = Br, R^1 = H; **c** R = OMe, R^1 = H; **d** R = Cl, R^1 = H; **e** R = Me, R^1 = H; **f** R = F, R^1 = H; **g** R = H, R^1 = Cl; **108** *n* = 2, 3; M = Ni, Cu; X = Cl, Br, I, ClO_4

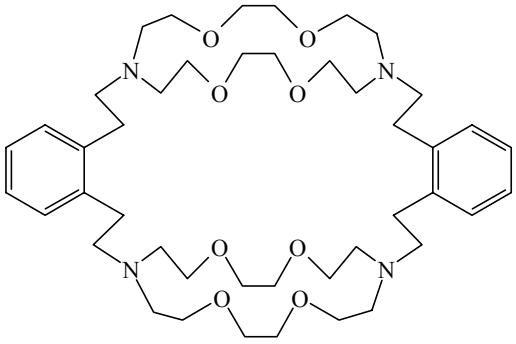
Examples of the production of complexes of macrocycles by the reaction of a metal salt with a ligand are given below.

The corresponding mononuclear inclusion complexes with the metal ion both inside and outside the cavity, depending on the nature of the counterion, can be obtained easily by the reaction of the azacryptand **5** [36] with Ni(II), Cu(II), Zn(II), and Cd(II) salts. The complexing ability of the macrocycles **13**, **14**, and **41** with a series of cations (Mg^{2+}, Li^+, Na^+, Ca^{2+}, Sr^{2+}, K^+, Ba^{2+}, NH_4^+, Cs^+) was studied [104]. The reaction of Zn(II), Cd(II), Ag(I), Pb(II), Co(II), Ni(II), and Cu(II) salts with the macrocycles **22** and **23** was investigated, and the stability constants of the obtained complexes were determined by potentiometry [105, 106]. The production of Cu(II), Co(II), and Ni(II) complexes of the macrocycles **52** and **53** was described in [69]. The structure of the complex [NiL][ClO_4], where L = **52**, was confirmed by X-ray crystallographic analysis. The reaction of the

macrocycle **109** (TMBC) with Cu(II) and Ni(II) salts in boiling ethanol gave the corresponding complexes $Cu(TMBC)(ClO_4)_2$, $Cu(TMBC)(N_3)(ClO_4)$, $Cu(TMBC)Br(ClO_4)$, $Cu(TMBC)I(ClO_4)$, $Cu(TMBC)(NO_3)_2$, $Ni(TMBC)(ClO_4)_2$, $Ni(TMBC)Br_2$, and $Ni(TMBC)(NO_3)_2$. X-ray crystallographic data were given for $Cu(TMBC)(N_3)(ClO_4)$ and $Cu(TMBC)(ClO_4)_2$. The kinetics of the formation of Ni(II) and Cu(II) complexes of the macrocycles **96** and **100** were investigated in [107].

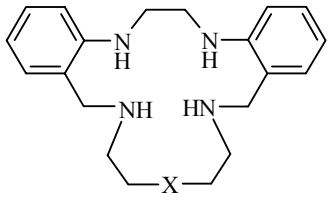


109 (TMBC)



110

The stability constant of the Rb(I) complex of the macrotricycle **110** was determined [108]. The reaction of the macrocycle **46** with $CrCl_3$ in the presence of triethylamine in benzene gave the corresponding mononuclear complex, for which X-ray crystallographic analysis was undertaken [109]. The formation of 1:1 Cu(II) complexes with the macrocycles **111a**,**b** was reported in [110]. The structure of the macrocycle **111b** and its Cu(II) complex was confirmed by X-ray crystallographic analysis.



111a,**b**

a X = O, **b** X = S

The synthesis and X-ray crystallographic data of the Ni(II) complexes of macrocycles **92a** and **93** were described in [111, 112], those of the Zn(II) complex of macrocycle **90** in [72], and those of the Ni(II) complex of macrocycle **55** in [114]. The stability constants of the 1:1 Zn(II) and Cd(II) complexes of macrocycles **91b**, **92a-c**, and **93** [97, 115] and the Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), and Pb(II) complexes of macrocycles **89** and **90** [114] were determined by a potentiometric method. The formation of Cu(II) and Ni(II) complexes of compounds **73b-d**,**g** was discussed in [83, 116], the Co(II) complexes of compounds **73b-d**,**g** in [59], and the Ni(II) and Co(II) complexes of the 22-membered macrocycles **78a-h** and **40** in [59, 85]. The luminescence spectral characteristics of the lanthanide ions (Eu^{3+}, Yb^{3+}) in complexes with the macrocycles **80b-d** and also with compounds **88a-c** were discussed in [117, 118]. A model was proposed for the structures [117] of the obtained Ln(III) complexes for the macrocycles **80b-d** (by analogy with that described in [119, 120]) (Fig. 4). Data from X-ray crystallographic analysis of the complex **57a** were given in [121]. Complex formation between Hg(II) and the macrocycle **29**, which is the aza analog of dibenzo-18-crown-6, in solution was investigated by ^1H and ^{13}C NMR methods [122]. The complexing characteristics of the macrocycles containing crown ether and thiocarbohydrazone fragments are interesting [123].

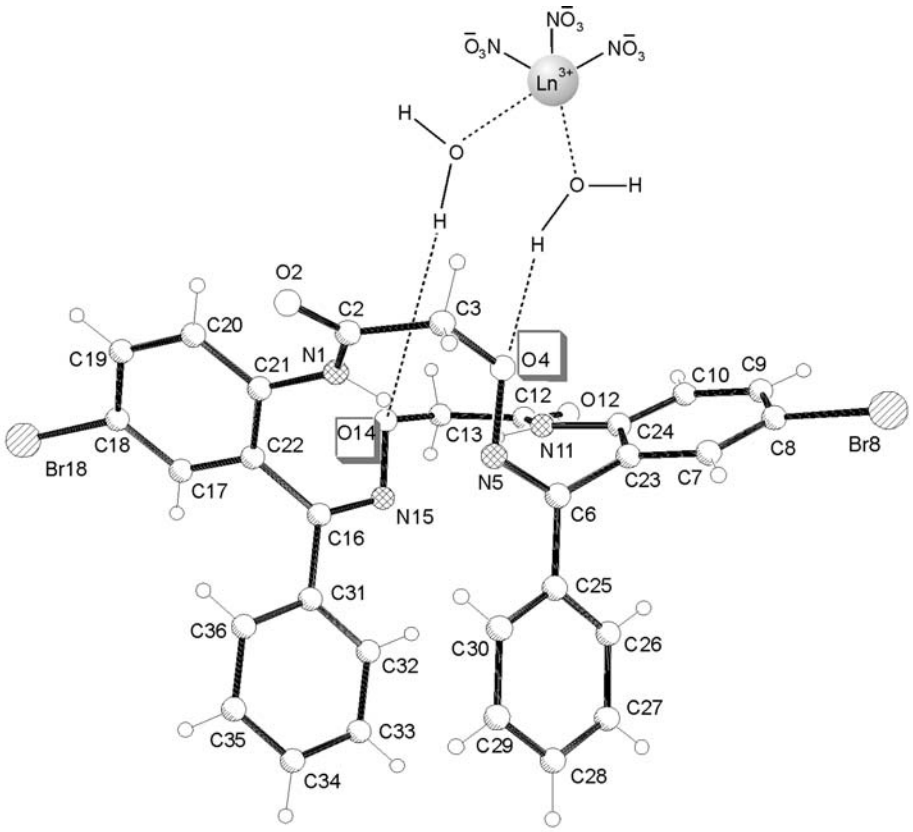
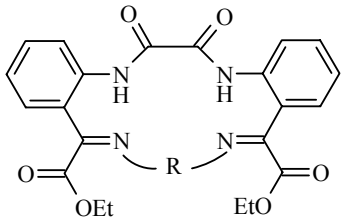


Fig. 4. A model of the structure of Ln(III) complexes of macrocycles **80b-d** (Ln^{3+} = Eu^{3+}, Yb^{3+}).

The dibenzotetraazamacroheterocycles are of interest in connection with the selectivity of their interaction with the ions of post-transition metals. The selectivity shows up to the greatest degree in the extraction variant of interaction of the metal with the dibenzotetraazamacroheterocycles. A series of publications have been devoted to aspects of the selective extraction of metal ions by macrocycles. Thus, it was observed that the heterocycle **29** extracts mercury selectively into organic solvents from aqueous solution [31]. In addition it was established that the metals Ag, Hg, Co, Cu, Ni, and Tl are extracted partially or completely by the macrocycles **4** and **29** at pH > 7 [32]. During investigation of the extraction of all alkaline-earth, transition, and rare-earth metals by compound **6** a high degree of extraction was observed for Pb(II) and relatively low values for Dy(III) [40]. Data from investigation of the extracting ability of macrocyclic Schiff bases toward transition metals (macrocycles **47a**,**c**,**d** and **48**) were presented in [67, 33, 124]. (Very high selectivity was observed for the macrocycle **47c** toward Cu(II).) The authors report on the use of the complex **98** [101] as ionophore in the polymer matrix of a Ni(II)-selective sensor. (The sensor was used successfully as indicator electrode during the potentiometric titration of Ni(II).) Similarly, 5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraazacyclotetradecane can be used as electroactive material in a membrane electrode for the determination of Cu(II) [125]. The study of complex formation in receptors of type **38a-e** is of considerable interest. Thus, complex formation with the cations of alkali metals (Li^+, Na^+, Rb^+, Cs^+), with the cations of ammonium salts (NH_4^+, $MeNH_3^+$, *t*-$BuNH_3^+$), and with aliphatic and aromatic diammonium cations [$^+H_3N(CH_2)_nNH_3^+$, (*n* = 3-9), *o*- and *p*-phenylenediammonium, etc.)] was investigated for compounds of this series [52, 54]. The strong bonding of dihydroxybenzenes (hydroquinone, pyrocatechol, and resorcinol) to receptors of the **38e** type was noted [126]. Complex formation with receptors based on glycoluril has also been described [55, 56, 58]. Information on the synthesis, bonding mechanism, and assembly of supramolecular objects based on glycoluril was reviewed in [127].

It is necessary to mention the successes of Chinese scientists, whose investigations in the field of supramolocular complexes containing amide and azomethine fragments can be regarded as a logical extension of the works of David Black. In these papers mononuclear complexes of type **68-70** are used as ligands for the creation of more complex supramolecular systems, study of the magnetic characteristics of which is of considerable interest (the design of novel magnetic materials). Thus, the synthesis of the first complex containing macrocyclic oxamide and μ-1,1- and μ-1,3-azide bridges $[Cu(L)Mn(N_3)_2]_n$ (H_2L = 2,3-dioxo-5,6:15,16-dibenzo-1,4,8,13-tetraazacyclopentadeca-7,13-diene). The synthesis of the complex was performed according to the "complex as ligand" principle described above. Many examples of the successful application of this approach are given below. Thus, the following products were synthesized on the basis of the mononuclear complexes of macrocyclic oxamides **112a-c** obtained according to the method in [129]: Tetranuclear complexes $[(CuL)_3Mn](ClO_4)_2$ (L = **112a**,**c**) [130], $[(CuL)_3Co](ClO_4)_2$ (L = **112a-c**) [34], $[(CuL)_3Fe](ClO_4)_3\cdot 3H_2O$ (L = **112a-c**) [131], $[(CuL)_3Ni](ClO_4)_2\cdot nH_2O$ (L = **112a-c**) [132], $[(CuL)_3Cr](ClO_4)_3\cdot 3H_2O$ (L = **112a-c**) [133]; binuclear complexes $[Cu(L)M(L_1)_n](ClO_4)_2$ (L = **112a**,**b**, L_1 = 1,10-phenanthroline and 2,2'-bipyridine, n = 1-2, M = Cu(II), Ni(II), Mn(II)) [134], $[Cu(L)Ni(L_1)NCS]ClO_4$ (L = **112a-c**, L_1 = N,N,N',N',N″-pentamethyldiethylenetriamine) [135], $[Cu(L)Ni(L_1)](ClO_4)_2\cdot H_2O$ (L = **112a**,**c**, L_1 = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [136].



112a–c

a R = $(CH_2)_2$, **b** R = $(CH_2)_3$, **c** R = $CH(Me)CH_2$

By using the Ni(II) complexes of the macrocycles **112a-c** as initial structural elements it was possible to obtain the binuclear complex $[Ag(NiL)(EtOH)(NO_3)]\cdot EtOH$ (L = **112c**) [137] and the trinuclear complexes $[Cu(NiL)_2(MeOH)_2](ClO_4)_2$ (L = **112a**) [138] and $[Mn(NiL)_2(EtOH)_2](ClO_4)_2$ (L = **112a**) [139]. The synthesis of the trinuclear complex $[Co(NiL)_2(H_2O)_2](ClO_4)_2$ (L = diethyl 5,6,7,8,16,17-hexahydro-6,7-dioxa-16H-dibenzo-[*e*,*n*][1,4,8,12]tetraazacyclopentadecyne-13,19-dicarboxylate) was described in [140], and that of the trinuclear complex $[Co(NiL)_2(H_2O)_2](ClO_4)_2\cdot 2EtOH$ [NiL = **69**, R = OMe] in [141].

The following products were synthesized from the complex **68** [M = Cu(II), n = 3]: The tetranuclear complex $[Mn(CuL)_3](ClO_4)_2$ [142], the tetrameric and pentameric complexes $[Cr(CuL(MeCN))(CuL(ClO_4))_2](ClO_4)\cdot 2MeCN$ and $[(H_2O)Gd(CuL)(CuL(MeOH))(CuL(ClO_4))_2](ClO_4)\cdot$ $\cdot MeOH\cdot H_2O$ [143], the pentanuclear complexes $[(CuL)_3(CuL(EtOH))La(H_2O)](ClO_4)_3\cdot 1.5H_2O$ [144] and $[(CuL)_3\{CuL(EtOH)\}Eu(H_2O)](ClO_4)_3\cdot 1.5H_2O$ and $[(CuL)_3\{CuL(EtOH)\}Tb(H_2O)](ClO_4)_3\cdot 2H_2O$ [145], and the polynuclear complex $\{[CuL(H_2O)](CuL)Mn(IM–2Py)\}\{[CuL(MeOH)](CuL)Mn(IM–2Py)\}(ClO_4)_4\cdot MeOH$ [146].

3. BIOLOGICAL ACTIVITY OF DIBENZOTETRAAZAMACROHETEROCYCLES AND THEIR COMPLEXES

The psychotropic characteristics of the macrocycles **73a-g** were studied in a search for new physiologically active compounds [83]. It was established that at doses of 1.85-3.20 mg/kg all the compounds **73a-g** exhibited clearly defined anticonvulsive activity in tests for antagonism with corazole and also protected

animals from tonic extensor spasms caused by the application of maximum electroshock (31-100 mg/kg). The most clearly defined anticonvulsive activity was exhibited by compound **73b**. It was noted that all the compounds **73a-g** had low toxicity. It was found that the macrocycles **78d-h** [85] in trials on mice reduced the aggressiveness of the animals compared with the control by 77% at doses of 25-50 mg/kg. The anticonvulsive action of compounds **78d-h** (in an antagonism test with corazole) appears at doses of 25-50 mg/kg, and there is no myorelaxant effect. All the macrocycles **78d-h** do not protect mice from convulsions caused by electroshock. Investigations into the characteristics of the macrocycles **80c**,**d** [88] in an antagonism test with corazole showed that these compounds have low psychotropic activity and in doses of 50 mg/kg protect mice from convulsions caused by corazole by 30%. It was also established that the macrocycle **80c** exhibits antiaggregation activity of IC_{50} $1 \cdot 10^{-4}$, which is ten times greater than for the acetylsalicylic acid widely used in medical practise as an antithrombotic agent. With $SnCl_2$ the macrocycles **94a**,**b** described above [50] give colored complexes of the $[Sn(N_4L)Cl_2]$ type (N_4L = **94a**,**b**). The complexes obtained in this way exhibit antibacterial activity [*Pseudomonas phaseolicola* (-), *Escherichia coli* (-)] and also have antifungal activity, while the metal chelates are more active than the tetraazamacrocycles. It was noted that the mononuclear complex of the macrocycle **33** of the $[Sn(N_4L)Cl_2]$ type, where N_4L = **33**, exhibits antimicrobial activity.

To sum up the foregoing discussion briefly it can be supposed that further investigations on dibenzotetraazamacroheterocycles will clearly embrace the principle of "synthetic macrocycles as structural elements of supramolecular systems" (molecular cells, chains, squares, dendrimers, sandwich structures). Such an approach is currently being pursued in the above-mentioned work by Chinese investigators and also in [147-153] and other papers.

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