

NONTRADITIONAL NITROGEN-CONTAINING MACROHETEROCYCLIC SYSTEMS WITH A  
HIGH DEGREE OF CONJUGATION (REVIEW)

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UDC 541.572.54:547.898

Methods for the classification and codification of the principal types of nitrogen-containing macroheterocyclic systems with a high degree of conjugation and the schemes for their synthesis are presented.

The heightened interest of researchers in nitrogen-containing macroheterocyclic compounds with a high degree of conjugation is due to the desire not only to **construct** effective models of natural porphyrin systems that display biological activity or to achieve the useful effects that are observed in the case of classical systems such as synthetic porphyrins and phthalocyanines or their analogs but also to create new macroheterocyclic systems that have substantially better characteristics.

Classification and Codification of Nitrogen-Containing Macroheterocyclic Systems with a High Degree of Conjugation

Mono-, di-, tri-, and macrocyclic systems differ with respect to the number of macroheterocycles capable of the independent formation of metal chelates that are included in the macroheterocyclic chelating agent. For such systems the most essential characteristics are the size, composition, and structure of the macrocyclic contour and the number and character of the donor atoms and the way in which they are arranged, as well as the order of arrangement of the structurally rigid constructive links.

The complete names of macroheterocyclic compounds are extremely unwieldy. Code designations that reflect the chief characteristics can be used for convenience and for hierarchical arrangement. Examples of the code designations of the most important types of **nitrogen-containing macroheterocyclic systems** with a high degree of conjugation are presented in Table 1. The number of links of the macroheterocyclic inner contour (in brackets) and the number of nitrogen atoms in the macroheterocycle (the nitrogen symbols with subscripts) occupy the central position in the code designation; the abbreviated designations of the condensed rings (in alphabetical order of the symbols on passing around the contour) are located to the left, while the **orders** of succession of the nitrogen atoms on passing around the inner contour are located on the right, followed by the total **numbers of  $\pi$  electrons** in the **systems** (this number functions partially as a control sum).

Synthesis of Monomacroheterocyclic Compounds with a High Degree of Conjugation

Nitrogen-containing monomacroheterocyclic compounds with a high degree of conjugation can be obtained by the following principal methods: 1) by the formation of the macroheterocyclic contour of a highly conjugated system; 2) by transformation of existing macroheterocyclic systems with an increase in the degree of **conjugation**; 3) by conversion of heterocyclic compounds to macroheterocyclic compounds.

Ring closure is the most widely used method for the preparation of macroheterocyclic compounds of the type under consideration. Synthetic schemes with the use of ring closure can be classified with respect to the number of linked identical or different structural fragments and their composition and structure. Examples of the classification of synthetic schemes on the basis of structural features of this sort are presented in **Table 1** in the second column. At a more profound level of classification one should take into account the types of reactions used, the types of reagents involved, and the conditions under which the preliminary and final reactions are carried out.

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All-Union Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances, Moscow 107258. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 1, pp. 3-18, January, 1982. Original article submitted May 11, 1981.

TABLE 1. Principal Types of Macroheterocyclic Systems with a High Degree of Conjugation Obtained by Macroring Closure

System code*	Synthetic scheme code	Template ions†	Literature
3B[12]N <sub>3</sub> , 1,5,9-24π	3([4]N)	Ni <sup>2+</sup> , Co <sup>3+</sup> , VO <sup>2+</sup>	[5-7]
2BPyl[12]N <sub>4</sub> , 1,4,7,10-24π	[5]N + [7]N <sub>3</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	[8]
2BIm[13]N <sub>4</sub> , 1,4,7,10-28π	[6]N + [7]N <sub>3</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	[9]
2BPyl[13]N <sub>5</sub> , 1,2,5,11-24π	[5]N + [8]N <sub>4</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	[8f]
3B[14]N <sub>2</sub> , 1,2-26π	[12] + [2]N <sub>2</sub>	NT	[10]
3BCh[14]N <sub>4</sub> , 1,2,5,8-26π	[2] + [12]N <sub>4</sub>	NT	[10]
4B[14]N <sub>4</sub> , 1,4,7,11-32π	[7]N + [7]N <sub>3</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	[8]
(Alk) <sub>2</sub> (CN) <sub>4</sub> [14]N <sub>4</sub> , 1,4,8,11-16π	2([3] + [4]N <sub>2</sub> )	NT; Ni <sup>2+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup> , etc.	[3, 11]
2B[14]N <sub>4</sub> , 1,4,8,11-24π	2([3] + [4]N <sub>2</sub> )	NT	[12]
	2([3] + [4]N <sub>2</sub> )	Ni <sup>2+</sup> , Cu <sup>2+</sup> , Co <sup>2+</sup>	[13-16]
	([3] + [11]N <sub>4</sub> )	Ni <sup>2+</sup>	[16]
	[4]N <sub>2</sub> + [10]N <sub>2</sub>	NT	[13]
	[3] + [11]N <sub>4</sub>	Ni <sup>2+</sup>	[14]
	[4]N <sub>2</sub> + [10]N <sub>2</sub>	Ni <sup>2+</sup>	[17, 18]
6,8-Me <sub>2</sub> B[14]N <sub>4</sub> , 1,4,8,11-24π	2([3] + [4]N <sub>2</sub> )	Ni <sup>2+</sup>	[17, 19, 20]
6,17-Me <sub>2</sub> B[14]N <sub>4</sub> , 1,4,8,11-24π	2([3] + [4]N <sub>2</sub> )	Ni <sup>2+</sup>	[21]
6,8,15,17-Me <sub>2</sub> B[14]N <sub>4</sub> , 1,4,8,11-24π	2([3] + [4]N <sub>2</sub> )	Ni <sup>2+</sup>	[21]
3B[14]N <sub>4</sub> , 1,4,8,11-26π	[2] + [12]N <sub>4</sub>	Ni <sup>2+</sup>	[22]
2BN[14]N <sub>4</sub> , 1,4,8,11-30π	[2] + [12]N <sub>4</sub>	Ni <sup>2+</sup>	[23]
B(2,3-Py)[14]N <sub>4</sub> , 1,4,8,11-24π	[4]N <sub>2</sub> + [10]N <sub>2</sub>	NT	[4f]
B2PyB2Py[14]N <sub>4</sub> , 1,4,8,11-32π	[6]N <sub>2</sub> + [8]N <sub>2</sub>	NT	[4f]
2(1,2-N)[14]N <sub>4</sub> , 1,4,8,11-32π	2([3] + [4]N <sub>2</sub> )	NT	[4f]
2(2,3-N)[14]N <sub>4</sub> , 1,4,8,11-32π	2([3] + [4]N <sub>2</sub> )	NT, Ni <sup>2+</sup> , Cu <sup>2+</sup> , etc.	[4f]
2Pz[14]N <sub>4</sub> , 1,4,8,11-24π	2([3] + [4]N <sub>2</sub> )	Ni <sup>2+</sup>	[24]
2Pz[14]N <sub>4</sub> , 1,4,8,11-24π	[1]N + [13]N <sub>5</sub>	NT	[25]
4B[14]N <sub>6</sub> , 1,2,3,8,9,10-32π	[6]N <sub>4</sub> + [8]N <sub>2</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup> , Co <sup>2+</sup>	[26]
B2Py[14]N <sub>6</sub> , 1,2,5,6,9,12-22π	2([7]N <sub>3</sub> )	Ni <sup>2+</sup>	[27, 28]
BPzBPz[14]N <sub>6</sub> , 1,2,5,6,9,12-32π	[4]N <sub>2</sub> + [10]N <sub>4</sub>	Ni <sup>2+</sup> , Pd <sup>2+</sup>	[29]
BPzQzPz[14]N <sub>6</sub> , 1,2,5,6,9,12-36π			

2B[14]N <sub>6</sub> 1,2,5,8,9,12—24π	2 ([7]N <sub>3</sub> )	Ni <sup>2+</sup>	[30]
3BPz[14]N <sub>6</sub> 1,2,5,8,9,12—32π	[6]N <sub>2</sub> + [8]N <sub>4</sub>	Ni <sup>2+</sup> , Pd <sup>2+</sup>	[31, 32]
2BPpPz[14]N <sub>6</sub> 1,2,5,8,9,12—32π	[6]N <sub>2</sub> + [8]N <sub>4</sub>	Ni <sup>2+</sup>	[33]
2B2Pz[14]N <sub>6</sub> 1,2,5,8,9,13—32π	[6]N <sub>2</sub> + [8]N <sub>4</sub>	Ni <sup>2+</sup>	[34]
2BPzQx[14]N <sub>6</sub> 1,2,5,8,9,12—36π	[6]N <sub>2</sub> + [8]N <sub>4</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup> , Pd <sup>2+</sup>	[35]
BPzBPz[14]N <sub>6</sub> 1,2,5,8,9,12—32π	2 ([7]N <sub>3</sub> )	Ni <sup>2+</sup> , Cu <sup>2+</sup>	[27, 28, 36—38]
1,2-NPy1,2-NPy[14]N <sub>6</sub> 1,2,5,8,9,12—40π	2 ([7]N <sub>3</sub> )	Ni <sup>2+</sup>	[39]
1,2-NQx1,2-NQx[14]N <sub>6</sub> 1,2,5,8,9,12—48π	2 ([7]N <sub>3</sub> )	Ni <sup>2+</sup> , Pd <sup>2+</sup>	[35]
2Py[14]N <sub>6</sub> 1,2,5,8,9,12—20π	2 ([2]N <sub>2</sub> + [5]N)	Fe <sup>2+</sup> , Mg <sup>2+</sup> , Zn <sup>2+</sup> , Sc <sup>3+</sup>	[40—42]
PyPzPyPz[14]N <sub>6</sub> 1,3,5,8,9,12—32π	2 ([7]N <sub>3</sub> )	Ni <sup>2+</sup> , Pd <sup>2+</sup> , Cu <sup>2+</sup> , Pt <sup>2+</sup> , Co <sup>3+</sup>	[43, 44]
B2PyB2Py[14]N <sub>6</sub> 1,3,5,8,10,12—32π	[6]N <sub>2</sub> + [8]N <sub>4</sub>	NT	[23]
4Py[14]N <sub>6</sub> 1,3,5,8,10,12—28π	2 ([7]N <sub>3</sub> )	NT	[45]
6,7,13,14-Me <sub>4</sub> [14]N <sub>6</sub> 1,2,4,5,8,9,11,12—16π	2 ([1]N + [6]N <sub>2</sub> )	Zn <sup>2+</sup>	[46]
3B[15]N <sub>4</sub> 1,4,8,12—28π	2 ([1] + [2] + 2[2]N <sub>2</sub> )	Ni <sup>2+</sup>	[47, 48]
4B[15]N <sub>6</sub> 1,2,5,9,13—32π	[4]N <sub>2</sub> + [11]N <sub>4</sub>	Ni <sup>2+</sup>	[49]
P3Py[15]N <sub>7</sub> 1,2,4,7,9,10,13—28π	[7]N + [8]N <sub>4</sub>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	[8]
3Py[15]N <sub>7</sub> 1,2,4,7,9,10,13—26π	[5]N + [10]N <sub>6</sub>	Fe <sup>2+</sup> , Mn <sup>2+</sup>	[26, 50—53]
4B[16]N <sub>4</sub> 1,5,9,13—32π	[5]N + [10]N <sub>6</sub>	Zn <sup>2+</sup>	[53, 54]
4Biv[16]N <sub>4</sub> 1,5,9,13—40π	4 ([4]N)	NT, Ni <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>2+</sup> , Pd <sup>2+</sup>	[55—59]
2(1,8-N)[16]N <sub>4</sub> 1,5,9,13—32π	2 ([4]N) + [8]N <sub>2</sub>	Pt <sup>2+</sup>	[60]
2BQxPz[16]N <sub>6</sub> 1,2,5,6,9,14—42π	4 ([4]N)	Cu <sup>2+</sup>	[2]
BPvBPv[18]N <sub>6</sub> 1,4,7,10,13,16—32π	2 ([3] + [5]N <sub>2</sub> )	Cu <sup>2+</sup>	[61]
Me <sub>3</sub> BPvBPv[18]N <sub>6</sub> 1,4,7,10,13,16—32π	[6]N <sub>2</sub> + [10]N <sub>4</sub>	Ni <sup>2+</sup> , Pd <sup>2+</sup>	[29]
6B[28]N <sub>4</sub> 1,4,15,18—52π	2 ([4]N <sub>2</sub> + [5]N)	Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Pb <sup>2+</sup>	[62, 63]
	2 ([4]N <sub>2</sub> + [5]N)	NT	[64]
	2 ([2] + [12]N <sub>2</sub> )	NT	[10]

\*Abbreviated designations of the condensed rings: B is benzene, Bim is benzimidazole, Ch is cyclohexane, In is indole, N is naphthalene, Py is pyridine, Pz is pyrazole, and Qx is 2,3-quinoxaline.

†Nontemplate synthesis is indicated by NT.

As applied to the synthesis of nitrogen-containing macroheterocyclic compounds with a high degree of conjugation, the reactions involved are presently limited to a small number of types. Reactions involving nucleophilic addition to multiple bonds (with or without subsequent splitting out of simple molecules) and nucleophilic substitution reactions are most often used; the formation of C=N bonds by the reaction of carbonyl compounds with a primary amino group is particularly popular.

Reactions involving macroring closure are most often carried out in the presence of **metal ions** (template synthesis). At present not enough study has been devoted to the mechanism of the template effect, and the template ions are chosen on the basis of general concepts of conformity with the dimensions of the coordination zone and mutual correspondences of the preferable stereochemistry of chelate formation. In a number of **cases nontemplates synthesis** does not take place at all. However, on the basis of the experimental data one should approach negative conclusions of this sort with a certain amount of caution, since one cannot be certain that the necessary conditions for carrying out the reactions were selected or that adequate detection methods were used.

Three principal types of template effects (TE), which have been arbitrarily called **kinetic**, **thermodynamic**, and **equilibrium TE**, have been proposed [1].

The kinetic TE is characterized by the feature that the reaction to form a macroheterocyclic compound does not occur without a metal ion. The metal ion coordinates the reagents in the necessary stereochemical orientation, thereby facilitating the occurrence of a number of regiospecific steps of the multistep reaction.

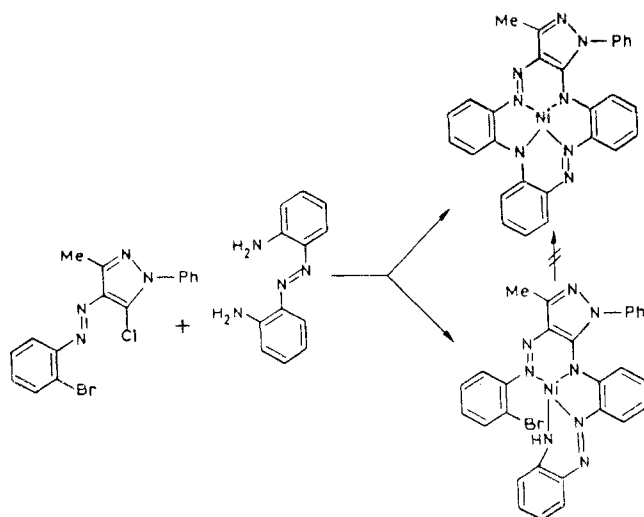
The thermodynamic TE is manifested when the reaction to form the macroheterocyclic compound can also occur in the absence of a metal ion; however, the latter, by bonding with the macrocyclic chelating agent, shifts the equilibrium to favor the formation of a metal chelate. As a result, the yield of the macroheterocyclic compound is increased as compared with the yield in nontemplate synthesis.

The equilibrium TE occurs in the case of the equilibrium formation of an intermediate, which, in the absence of a metal ion, is converted irreversibly to a nonmacrocyclic product; in the presence of a metal ion this intermediate forms a stable complex with it, and the reaction proceeds further to give a macrocyclic metal chelate.

Most of the experimental facts are in agreement with these types of TE, but there are evidently also modifications of these types of TE or some other types of TE. Thus the parallel formation of a macrocyclic chelating agent and its metal chelate with the template ion [2] can be regarded as a modification of the thermodynamic TE. Template ions that are smaller or larger than a certain value, by functioning as an organizing agent, cannot enter the coordination vacancy of the final macroheterocycle. In the synthesis of 6,13-dialkyl-2,3,9,10-tetracyano-1,8-dihydro-1,4,8,11-tetraazacyclotetradecenes [3] the nontemplate process gave the products in low yields,  $Mg^{2+}$ ,  $Mn^{2+}$ , and  $Cr^{3+}$  template ions increased the yields of the free chelating agents, while ring closure was accompanied by the formation of the corresponding metal chelates in the presence of  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ , and  $Zn^{2+}$  ions. The addition of chromium(III) acetate also stimulated the formation of the analogous free diareno[b,i][1,4,8,11]tetraazacyclotetradecene chelating agents [4].

Template double diazo coupling at one carbon atom, which leads to hybrid crown formazans [65], is accompanied by ejection of the template ion, as a result of which the free chelating agent is formed. Here we are probably dealing with a new type of TE in which the template ion promotes ring closure through the formation of a highly reactive nonmacrocyclic metal chelate intermediate but is subsequently not retained by the macrocyclic ligand.

In the synthesis of macroheterocyclic compounds by the reaction of several reagent-chelates the template ion may promote the formation of a macrocyclic metal chelate and **simultaneously stop** the cyclization process by the formation of "undercyclized" nonmacroheterocyclic metal chelates that are incapable of further cyclization under the reaction conditions. This sort of negative TE may occur when macroring closure requires the synchronous occurrence of two or several reactions between ligands that are incorporated in the metal chelate intermediate. Thus a macroheterocyclic [1,2,5,8,9,12]hexaazacyclotetradecenate chelate of nickel and a nonmacroheterocyclic chelate of a bisazo compound are formed simultaneously in the reaction of 4-(2-bromophenylazo)-5-chloro-3-methyl-1-phenylpyrazole with 2,2'-diaminoazobenzene in dimethylformamide (DMF) in the presence of Ni(II) salts and potassium carbonate; the latter product does not undergo cyclization under the conditions of this reaction [31] (see [38]).



The synthesis of 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecene and its derivatives has been of considerable interest to researchers, and the largest number of variants has been developed for the 2([3]+[4]N<sub>2</sub>) scheme. In this scheme the o-arylenediamine fragment changed only slightly, and various acyclic and heterocyclic reagents — propynal [4,12, 13,66], 1,1,3,3-tetramethoxypropane [15, 16], substituted malondialdehydes [61, 67-70], 3-chloroacroleins [71], 3-ethoxyacroleins [24, 72, 73], 1,3-diketones [14, 17, 20, 74], and 4-aryl-1,2-dithiolium salts [75] — were used as the three-carbon component.

Methods in which propynal, meso-substituted malondialdehydes, and 1,2-dithiolium salts are used are attractive in that they make it possible to realize nontemplate syntheses. The use of substituted 1,3-diketones has limitations: Macrocyclic products are obtained when the meso substituents are halogen atoms [61, 74] or acyl [17, 74], arylazo [74, 76], cyanomethyl [74], and carbethoxymethyl [74] groups but not when they are alkyl groups (when they do not form five- or six-membered rings with the extreme substituent [74]). An increase in the volume of the extreme substituents in 1,3-diketones slows down cyclization, while 2,6-dimethyl- and 2,2,6,6-tetramethyl-3,5-heptanediones do not form tetraazacyclotetradecene systems [74].

Stopping the reaction at the step involving the formation of [10]N<sub>2</sub>- [17] or [11]N<sub>4</sub>- quadridentate intermediates [14] can be used for the synthesis of unsymmetrical tetraazacyclotetradecenes [4, 14, 17, 18].

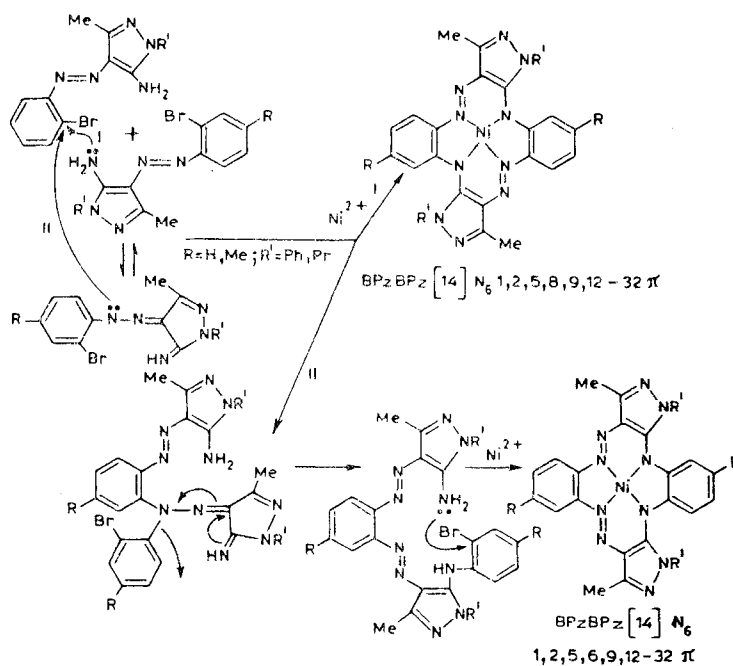
2,6-Diacetylpyridine [5]N [8, 26, 40, 41, 62-64] and 2,9-diacetyl-1,10-phenanthroline [8]N<sub>2</sub> components [26] and other diacyl derivatives of the aromatic [8] and heteroaromatic [9] series have found extensive application in the synthesis of quadri-, quinq-, and sexidentate macroheterocyclic compounds with azomethine bonds.

Template cyclizations with diamine components are, as a rule, most easily realized on Ni(II) and Cu(II) ions, which prefer square-planar coordination. It has been found that Co<sup>2+</sup> [8], Zn<sup>2+</sup> [26, 63], and Mn<sup>2+</sup> [26, 63] ions are sometimes ineffective. It has been established that Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, and Pb<sup>2+</sup> ions are suitable in the template cyclization of 2,6-diformylpyridine with o-phenylenediamine, while transition metal Mn<sup>2+</sup>-Zn<sup>2+</sup> ions, as well as Mg<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup> ions, are ineffective (although a cadmium chelate can be obtained from the barium chelate by an exchange reaction). In the case of similar cyclization with 2,6-diacetylpyridine the barium ion proved to be ineffective [62].

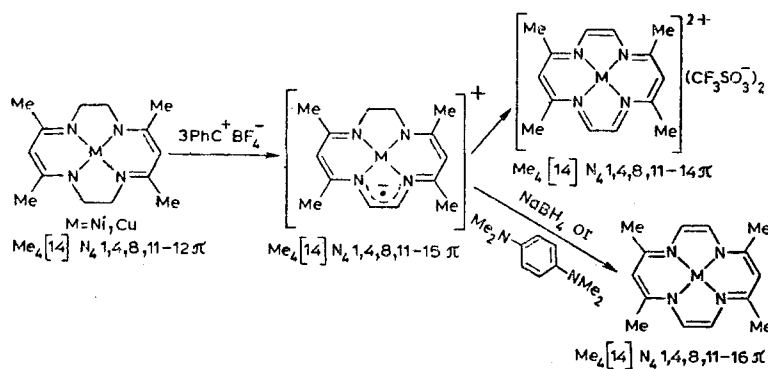
In connection with the relatively low chemical and photochemical stability of macroheterocyclic compounds that contain an azomethine bond, the synthesis of more stable compounds, viz., macroheterocyclic derivatives of 1,10-phenanthroline [23, 45] and 2,2'-bipyridyl [46] and macroheterocyclic bisazo compounds [27-29, 31-39, 43, 44], has proved to be timely. In these cases nucleophilic substitution of halogen atoms by aryl- or hetarylamino groups was used, which, as a rule, required relatively severe conditions. Even more severe conditions, viz., heating to 230-260°C, were required for nontemplate synthesis with replacement of halogen by a carbon-containing group in the synthesis of the B2PyB2Py [14] N<sub>4</sub>1,4,8,11-32π system [23].

The necessity for carrying out template syntheses of this sort at increased temperatures is a certain limitation of the method and sometimes leads to the formation of unexpected reaction products. Thus 5-amino-4-(2-haloarylo)pyrazoles exist in equilibrium with hydrazone tautomers, and, in addition to normal replacement of the halogen by an arylamino group, which is associated with an increase in the lability of the halogen under the influence of the o-azo group, in the case of template cyclization at  $\sim 130^\circ\text{C}$  one also **observes** replacement of halogen by an arylhydrazone group with subsequent migration of the aryl group of the hydrazone form from the nitrogen atom to the 4 position to the nitrogen atom in the 5 position of the pyrazole ring, which culminates in further cyclization to the isomeric cisoid bisazomacrocyclic [14] $N_6$ 1,2,5,6,9,12 compound [27, 28].

It is expedient to use the transformation of previously prepared macroheterocyclic compounds with an increase in the degree of conjugation in cases in which the incompletely conjugated macroheterocycles are more accessible. For this, oxidative dehydrogenation of the ligand is most often used.

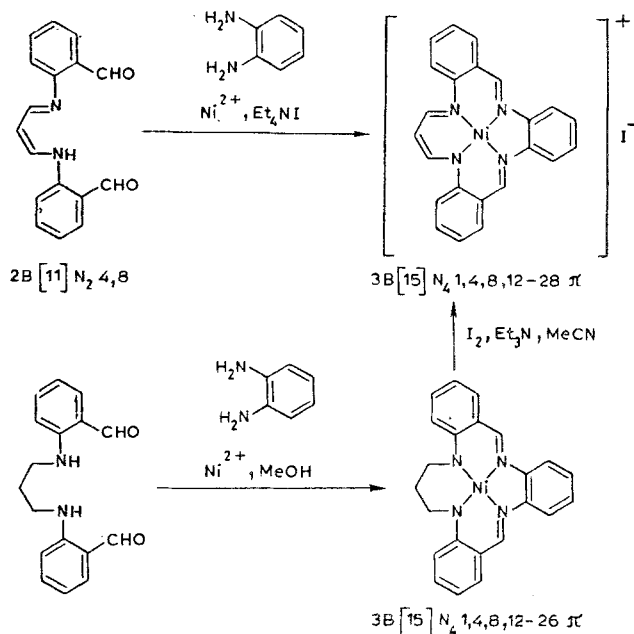


The partially conjugated  $\text{Me}_4[14]N_4$ 1,4,8,11-12 $\pi$  system is readily dehydrogenated by trityl tetrafluoroborate to give a 15 $\pi$  cation radical [77-79], which can be subsequently oxidized to a doubly charged 14 $\pi$  cation [77, 80] or transformed to the corresponding 16 $\pi$  neutral complex [77, 80].



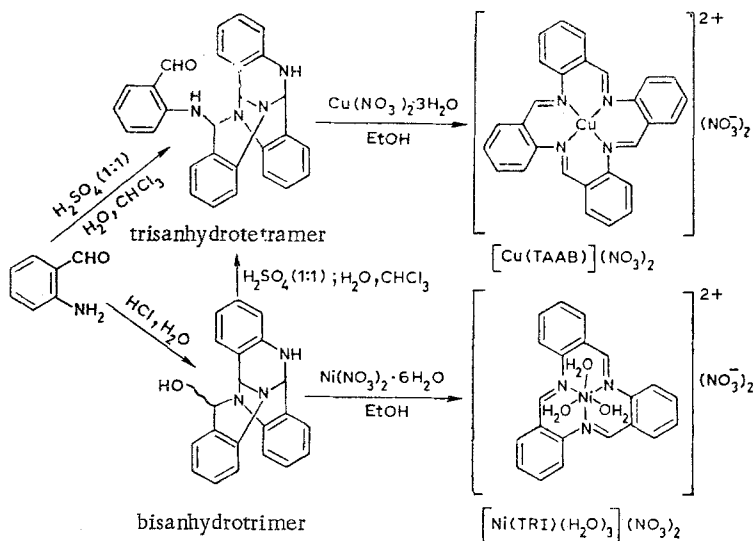
The 3B[15] $N_4$ 1,4,8,12-28 $\pi$  system can be obtained by the template reaction of dialdehyde 2B[11] $N_2$ 4,8 with *o*-phenylenediamine. The method requires the strict observance of anhydrous conditions [49]. The same system can be obtained from the more accessible dialdehyde through partially conjugated chelate 3B[15] $N_4$ 1,4,8,12-26 $\pi$  by oxidative dehydrogenation of the ligand [81].

Oxidative dehydrogenation of the ligand has also been widely used in the preparation of 1,2,4,5,8,9,11,12-octaazacyclotetradecene systems [47, 82, 83].

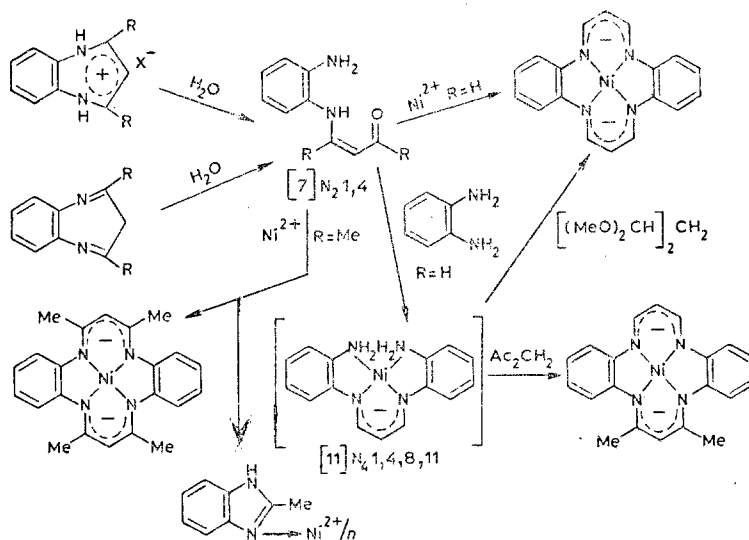


The conversion of heterocyclic compounds to macroheterocyclic compounds can be realized by opening the heterorings with subsequent rearrangement and dehydration, opening of the heteroring to give a reagent that is capable of forming a macroring with another component, or by means of cleavage of one or several internal bonds of the polycyclic system.

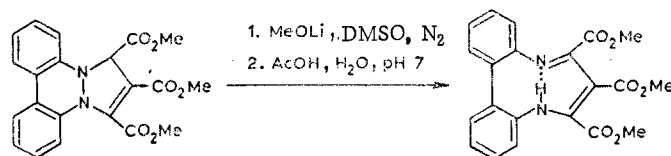
Depending on the reaction conditions, the self-cyclization of 2-aminobenzaldehyde gives different mixtures of polycyclic products, by treatment of which with salts of transition metals in ethanol individual metal chelates can be obtained as a result of hydrolytic ring opening, rearrangement, and template cyclization [5, 84].



2,4-Dimethyl-3H-1,5-benzodiazepine [85] or 1,5-benzodiazepinium cations [14, 85] undergo hydrolytic opening of the seven-membered ring to give a tridentate  $[7]N_{2,1,4}$  intermediate, which in the template process may undergo further transformation ( $R = Me$ ) to macrocyclic metal chelate  $Me_4 2B [14] N_{4,1,4,8,11-24 \pi}$  and simultaneously to a 2-methylbenzimidazole complex. In the presence of *o*-phenylenediamine and a nickel salt one observes the formation ( $R = H$ ) of macrocyclic quadridentate intermediate  $[11]N_{4,1,4,8,11}$ , which upon reaction with the corresponding three-carbon component can be subsequently converted to the symmetrical or unsymmetrical macrocyclic  $[14]N_{4,1,4,8,11}$  system [14].



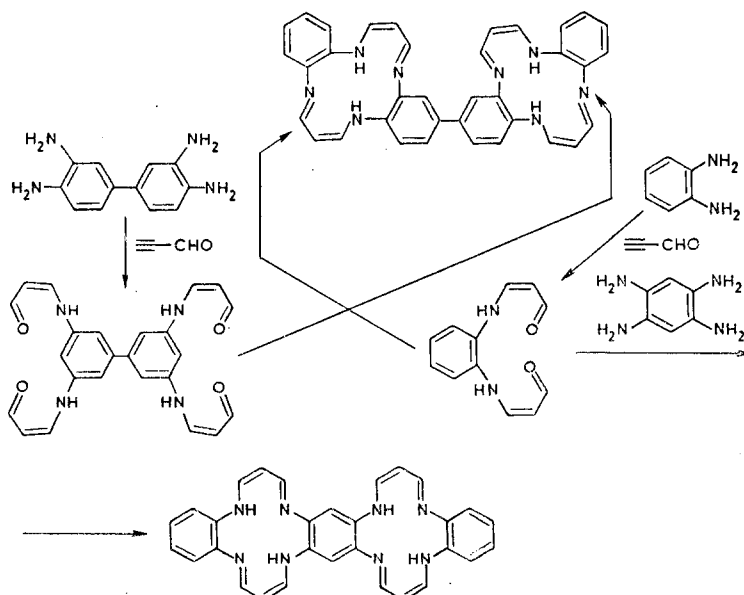
Some polynuclear heterocyclic systems can be converted to macroheterocyclic systems by cleavage of one or several inner bonds of the system. The method is illustrated by the formation of the 2B[9]N<sub>2</sub>1,5 system [86]:



### Synthesis of Di- and Polymacroheterocyclic Systems

Di- and polymacroheterocyclic systems with a high degree of conjugation can be synthesized by repeated cyclization of specially selected polyfunctional components or by the conversion of monomacroheterocyclic systems.

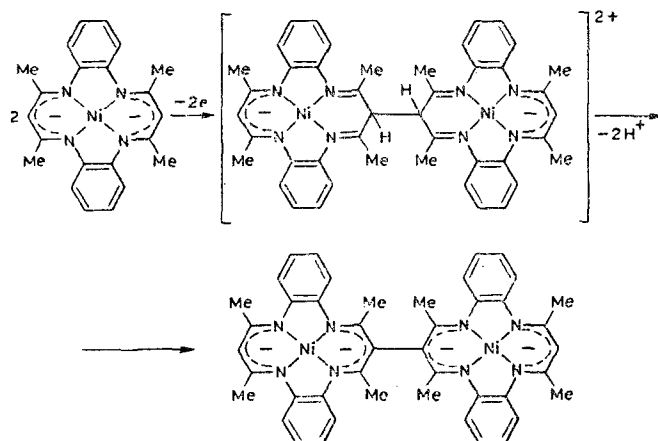
The reaction of aromatic di- and tetraamines with the products of condensation of di- and tetraamines with propynal leads [22, 87] to dimacroheterocyclic compounds that contain two  $[14]N_{4,1,4,8,11}$  systems:





Similar methods (the template method or methods based on free chelating agents) have been used in the synthesis of the corresponding di- and polymacrocylic metal chelates of copper, nickel, cobalt, and iron(II) [22, 87].

Dimacroheterocyclic compounds have been obtained from monomacroheterocyclic compounds by chemical [88] and electrochemical [89] oxidative CC coupling in the meso position;



### Reactions of Macroheterocyclic Compounds

Nitrogen-containing macroheterocyclic compounds with a high degree of conjugation undergo reactions that involve centers that enter the coordination zone directly, centers on the periphery, and coordination and peripheral centers simultaneously.

Whereas metal chelates of macroheterocyclic compounds with a reduced degree of conjugation are demetallated by the action of acids or cyanides, demetallation becomes more difficult as the **degree** of conjugation increases. In addition, since template synthesis, which terminates with the formation of macrocyclic metal chelates, may in many cases be the only source of a macroheterocyclic system, the development of new demetallation methods is an urgent problem.

Metal chelates of azomethine [14] $N_4$ 1,4,8,11-tetraazacyclotetradecene systems are demetallated by treatment with hydrogen halides in an alcoholic medium [20, 67]. The similarly constructed hexaazacyclotetradecene metal chelates are resistant to the action of many agents [31, 32, 34, 36, 37, 43].

The problems of axial ligation for this class of compounds have not been subjected to a special systematic study. The increased interest in the axial ligation of 6,8,15,17-tetramethyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecenates of transition metal ions [50, 67, 90-94] is associated with the unusual coordination of this ligand, which, for steric reasons, takes on a saddle-shaped configuration [91-93, 95]. In this system the metal ion that participates in coordination deviates from the  $N_4$  plane, and this is frequently **accompanied by the** formation of pentacoordinated compounds [90, 91, 93, 96, 97]. The degree of deviation from the  $N_4$  plane in high- and low-spin complexes depends on the character of the axial ligand [91, 92, 94].

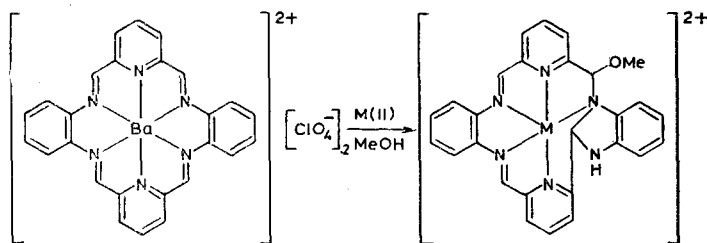
Interesting M-alkylation and M-arylation reactions at the central rings of macroheterocyclic chelates have been observed [97] in the reaction of alkyls and arylhydrazines in the presence of oxidizing agents with 3,4,10,11-tetramethyl-1,8-dihydro-1,2,5,6,8,9,12,13-octaazacyclotetradecenato(2-)cobalt and 6,8,15,17-tetramethyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecenato(2-)(thiocyanato)iron.

Macroheterocyclic compounds that contain a 1,5-diaza-1,3-pentadiene chain in the **coordination contour** readily undergo electrophilic substitution with incorporation of a substituent in the meso position. Bromination [98], acylation [99-101], and diazo coupling [102, 103] have been carried with 5,14-dihydrobenzo[b,i][1,4,8,11]tetraazacyclotetradene [99] and its 6,8,15,17-tetramethyl-substituted derivatives [101, 102] and their nickel chelates [98, 100, 103]. Mono-meso-substituted compounds [99-101] have been obtained in a number of cases.

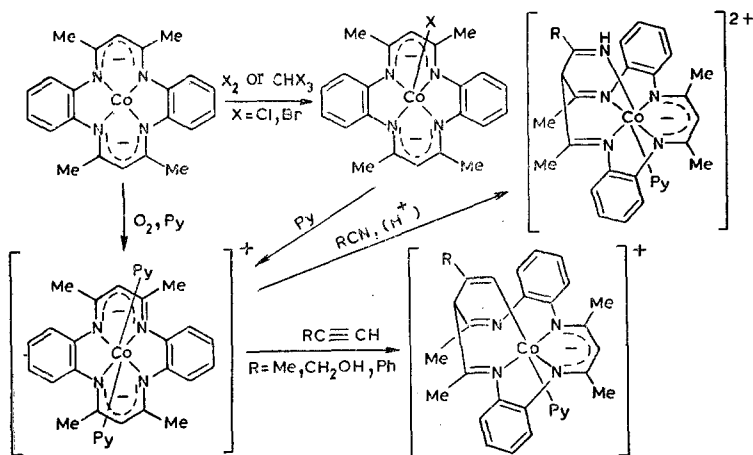
"Covered" or "basket-shaped" derivatives of this system were obtained in [100] by reaction with acid dichlorides.

Nucleophilic addition of alkoxy and substituted amino groups is characteristic for macroheterocyclic compounds that contain an azomethine group in the coordination contour. This sort of reaction has been studied in greatest detail in the case of nickel and copper chelates of the 4B[16]N<sub>4</sub>1,5,9,13-32π-TAAB system [104-106], in which "basket-shaped" pentacoordinated compounds with a donor atom in the middle of the incorporated chain were obtained [105, 106]. A "basket-shaped" compound with a 1,8-diazooctane chain was recently obtained [107].

Contraction of an eighteen-membered macroring to a fifteen-membered macroring was observed in the reaction of the barium chelate of BPyBPy[18]N<sub>4</sub>1,4,7,10,13,16-32π with Mn(II), Fe(II), Co(II), and Zn(II) salts in refluxing methanol [108]:



It has been found that reactions that simultaneously involve coordination and peripheral centers can be realized in the case of derivatives of dibenzotetraazacyclotetradeceno(2-) cobalt [90, 109].



The investigation of redox reactions by means of electrochemical and spectral methods has been carried out most extensively in the case of tetraaza- and octaazacyclotetradecenes in order to establish the fine structures of the isomers [83] and products formed in successive steps of electrochemical transformations [77, 79, 110-112].

The oxidation of 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecenates with iodine gives products with the general formula  $[ML]I_x$ , where  $x$  varies from 1 to ~3 and may be a fractional number. Strong electron-acceptor substituents in the benzene rings or in the meso position of the 1,5-diazapentadiene chain hinder oxidation with iodine, while electron-donor substituents facilitate it. Data from EPR spectroscopy indicate that during oxidation electrons are removed mainly from the ligand-center orbitals to give  $\pi$  radical cations [16, 70, 113]. Products of a similar type have also been obtained with 4B[16]N<sub>4</sub>1,5,9,13 chelates [114].

Tetracyanoquinodimethane and bis[1,2-ethenedithiolato(2-)-S,S]nickelate react with 1,8-dihydro-5,7,12,14-tetramethyl[1,4,8,11]tetraazacyclotetradeceno(2-)nickel to give  $\pi$ -donor-acceptor complexes that display semiconductor properties [115].

Nitrogen-containing macroheterocyclic compounds of the type under consideration have shown some promise in the modeling of a number of biologically important systems. The structural prerequisites for the escape of the high-spin Fe(II) ion from the cavity of the **coordination contour** and for the incorporation of an Fe(II) ion in the case of spin pairing — a **process that** is an integral part of the proposed mechanism for oxygen transport by hemoglobin [116] — in addition to porphyrin systems, have been investigated in the case of the saddle-shaped  $\text{Me}_4\text{2B}[14]\text{N}_4\text{1,4,8,11-}24\pi$  [95] and shielded (in the coordination zone)  $[14]\text{N}_8\text{1,2,4,5,8,9,11,12-}16\pi$  [117-119] systems and in the case of a system with an expanded contour, viz.,  $\text{Me}_4\text{-B3Py}[15]\text{N}_7\text{1,2,4,7,9,10,13-}28\pi$  [51].

In connection with the development of fuel cells considerable interest is being directed to macrocyclic metal chelate catalysts for the electrochemical oxidation of various substances; with respect to its activity, dihydrodibenzotetraazacyclotetradeceno(2-)-cobalt is one of the most important compounds [120, 121]. The same catalyst displays high activity in the cathode reduction of oxygen [122, 123]. However, it has been noted [124] that this activity is lost in the course of a few hours.

The same chelates of macroheterocycles catalyze the oxidation by oxygen in the presence of chloranil or its analogs of di- and triarylmethanes to di- and triarylcation salts [125, 126] and, **when an o-carboxy group is present**, to lactones [127]. In the presence of pyridine dibenzotetraazacyclotetradeceno(2-)-cobalt catalyzes the oxidation of ethylbenzene to acetophenone by means of oxygen [22].

Nickel chelates of  $2\text{B}[14]\text{N}_4\text{1,4,8,11}$  [76],  $\text{BN}[15]\text{N}_4\text{1,4,8,12}$ , and  $2\text{N}[16]\text{N}_4\text{1,5,9,13}$  [128] systems, which contain two arylazo groups in the meso positions of 1,5-diazapentadiene chains, have been proposed as dyes with red and brown hues for polyvinyl chloride. However, it was later demonstrated that metal chelate dyes of this sort have relatively low chemical and photochemical stabilities [129].

Nickel(II) hexaazacyclotetradecenates of the  $\text{BPzBPz}[14]\text{N}_6\text{1,2,5,8,9,12}$  type have been proposed as highly light- and heat-resistant dyes with **bright-green** hues for polyamides [130]. The dyes are soluble in fused polyamides and are stable in them for a long time.

Iodine-containing products of the oxidation of dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecenes and their metal chelates have relatively high electrical conductivities (up to  $4.5 \cdot 10^{-1} \text{ mho-cm}^{-1}$  in the powdered state [114] and up to  $240 \text{ mho-cm}^{-1}$  in the crystalline state [70] at room temperature). A significant change in the electrical conductivity is noted in the case of the  $[\text{Pd}(\text{TAAB})][\text{I}_3]_{2.7}$  complex when the pressure is increased [113].

The outlook is favorable for the use of macroheterocyclic compounds of the type under consideration in analytical chemistry and separatory technique [131]. **6,8,15,17-Tetramethyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecene has been recommended for the spectrophotometric determination of copper in aluminum alloys** [132].

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SYNTHESIS OF 4,5-DIHYDROFURAN DERIVATIVES BY THE REACTION OF  
ACETOACETIC ESTER WITH CONJUGATED ALKENYNES\*

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UDC 547.722.3.07

The regiochemistry of the reaction of acetoacetic ester with vinylacetylene, isopropenylacetylene, and vinylisopropenylacetylene in the presence of the manganese acetate/copper acetate oxidative system was studied. Derivatives of furan and 4,5-dihydrofuran were obtained as a result of oxidative cyclization of intermediate radicals that contain unsaturated groups in the  $\alpha$  position. Data from the IR, UV, PMR,  $^{13}\text{C}$  NMR, and mass spectra of the synthesized compounds are presented.

We have recently studied the reaction of conjugated alkenes with acetylacetone in the presence of the manganese(III) acetate/copper(II) acetate oxidative system [2]. We showed, in particular, that the reaction of the acetylacetyl radical with vinylacetylene proceeds nonregioselectively and that the intermediate reaction particles, which contain unsaturated groups in the  $\alpha$  position, are stabilized exclusively via a cyclization pathway that leads to the formation of dihydrofuran and furan derivatives.

\*Communication 75 from the series "Reactions of Unsaturated Compounds." See [1] for Communication 74.

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Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 1, pp. 19-23, January, 1982.  
Original article submitted November 4, 1980; revision submitted June 17, 1981.