



CORROLES AS AROMATIC ANALOGS OF CORRINOIDS AND VITAMIN B₁₂: SYNTHESIS, STRUCTURAL FEATURES AND MACROCYCLE PROPERTIES, PERSPECTIVES OF MATERIAL CHEMISTRY ON CORROLE BASIS

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Keywords:

tetrapyrrolic macroheterocyclic compounds; porphyrins; corroles; synthesis; spectral characteristics; acid-basic and coordinating properties; metallocomplexes; catalysis; photodynamic therapy

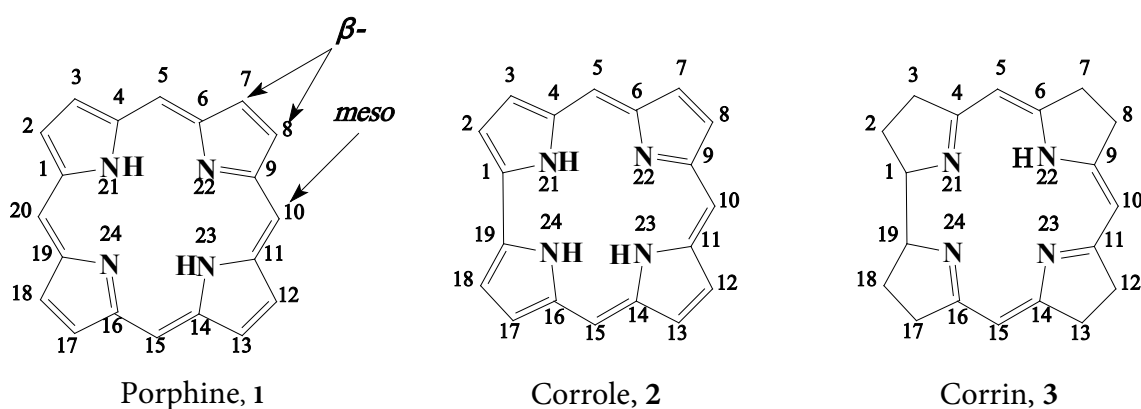
The review deals with literature and own experimental data for synthesis, structural features, spectral, acid-basic and coordinating properties of aromatic macroheterocycles – corroles. Perspectives of practical application of these compounds are considered briefly. Relationship between corrole properties and its geometrical and π -electronic structure is demonstrated. It is shown that corroles have number of features and unique characteristics in despite of insignificant change of structure compared to the most studied class of macroheterocyclic compounds – porphyrins.

Introduction

Over the past few decades, researchers from various countries have been conducting in-depth research on heterocyclic macrocycle compounds with various structures, first of all porphyrins and their analogues [1–9]. The molecule of the simplest porphyrin, porphine (**1**), is an 18-electronic aromatic fused π -system, which consists of four pyrrole rings connected to each other by methine (=CH-) bridges. Porphine can be considered a product of oxidative condensation of four pyrrole molecules with four formaldehyde molecules. It can indeed be derived from these compounds, but is formed with a low yield of only about 1-2% [1–4]. Porphyrins (H₂P) are products of substitution of hydrogen atoms at the edge of porphine macrocycle at β -positions (in pyrrole rings) or at *meso*-positions (at methine bridges between pyrrole rings); there are also mixed substitution porphyrins, in which the substituents exist both



in β -, and *meso*-positions of a molecule. Currently, a large number of natural and synthetic porphyrins are known, as well as their analogues – porphyrinoids – compounds related to H_2P . The difference between porphyrinoids and porphyrins lies in the structure of the outer ring of a macrocycle and/or the inner coordination cavity of a molecule [10–14]. The interest in these compounds was initially due to their great biological importance in nature – porphyrins include blood heme and green leaf chlorophyll, and porphyrin fragments exist in some enzymes (for example, cytochromes involved in the Krebs cycle and providing cell respiration) [2, 5–7]. Later it was found that not only natural, but also synthetic H_2P have interesting applied properties and can be used in various fields – catalysis, medicine, production of optical materials, sensors, semiconductors, pigments etc. [5, 15, 16]. The complexity of the synthesis of H_2P and related compounds on an industrial scale is a factor that significantly limits their wide application. However, the interest in porphyrins and their analogues is not fading (Fig. 1), and new representatives of this class of compounds with a unique set of properties are synthesized [6, 7].



Sometimes even a slight modification of the carbon skeleton of the macrocycle, the internal coordination cavity or the periphery of the molecule leads to a very significant change in the properties of the compound. One of the best examples of this statement is chemistry of corroles. [12, 16–33].

Corroles, 2 (H_3Cor) are tetrapyrrole macrocyclic porphyrin-like compounds. They have three *meso*-methine bridges and one direct pyrrole-pyrrole bond. This bond is formed because there is no carbon atom in one of *meso*-positions of the macrocycle. The corroles can be considered structurally an intermediate link between porphyrins and corrins – compounds related to vitamin B_{12} . Carbon skeleton of a molecule is similar to corrins (3), but unlike them and similarly to porphyrins, corroles are aromatic compounds [14, 34].

The studies of β -octaalkyl-substituted corroles were started in 1965. [35]. These compounds have sparked the interest of scientists due to the similarity of the carbon skeleton molecule to the corrin nucleus of the vitamin B_{12} molecule. Corroles were considered as possible synthetic precursors for producing cobalamin. However, attempts to synthesize vitamin B_{12} from corroles were unsuccessful. Moreover, obtaining the corroles proved to be very time



consuming due to the lack of proven synthesis techniques and commercially available reagents. Therefore, up until the mid-1990s, the chemistry of corroles did not attract much attention.

In 1993-94, corrole synthesis methods were proposed as complexes of cobalt and triphenylphosphine with mixed type of substitution [36, 37]. The situation changed radically in 1999. It was the year of first reports of synthesis of *meso*-substituted corroles without substituents in β -positions of molecules [38, 39]. The new structural group of compounds proved to be much more easily accessible synthetically, which contributed to a new surge of interest in the chemistry of corroles. According to the international database PubMed, there are currently at least a few dozen articles on this topic published on this topic (Fig. 1). It's important to notice that the database takes into account only medical articles (the total number of publications is actually greater). It was found that H_3Cor are superior to H_2P in many respects, mainly in stability and reactivity of complexes with transition metals in high oxidation degrees [21, 22, 25, 27]. Stabilization of unusual degrees of oxidation of metals in the complexes leads to non-innocence of corrole-ligands – the possibility of reversible electron exchange between the metal-complexer and ligand. These electronic transitions lead to a change in the formal degree of oxidation of the metal center and the transition of the ligand into a radical form [26, 27, 31, 32, 40].

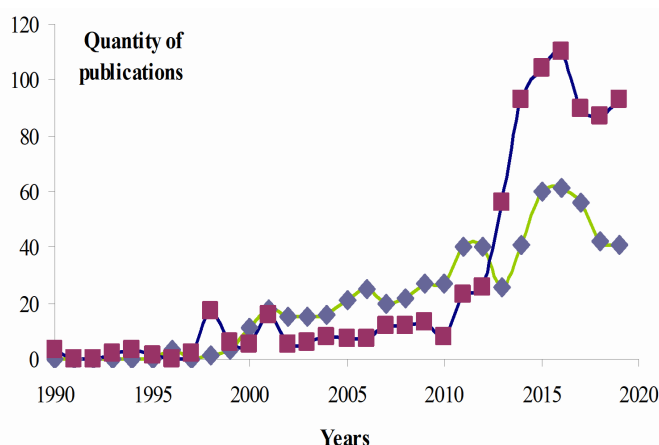


Fig. 1. Annual number of publications of topic by the data of PubMed (1 – search for key word «corrole»; 2 – search for key word «porphyrinoid»)

medical and environmental problems. Corroles can be used in converting light energy into electricity as a component of solar cells. The use of corroles for diagnostics and photodynamic therapy of tumors, as well as inactivators of active oxygen and its peroxide forms in the body is promising [13, 15, 16, 22].

In addition to the most typical reactions of acid-base interaction and complex formation, a number of reactions rare for H_2P were found for H_3Cor at the edge of the macrocycle. Moreover, the behavior of corroles has a lot of specific aspects even in the same reactions as porphyrins. This fact together with the increased chemical activity of the corroles, makes them one of the most interesting research subjects in the chemistry of heterocyclic macrocyclic compounds.

It turned out that the corroles have unusual photophysical characteristics and have high NH-acidity. They also show catalytic properties in the form of complexes in a number of processes such as hydroxylation and epoxidation of organic substrates, the formation of aziridine derivatives, the transfer of groups from one substrate to another, the oxidation of phosphines and carbon monoxide, etc. Corrole-based sensor models have been created to solve



Distinctive structural features of corroles as aromatic heterocyclic macrocycles. The variety of structural groups of corroles

Using a combination of spectral, structural, and other physical-chemical methods, it was found [18, 19, 24, 26-28, 30, 32, 33] that H₃Cor have a number of features of geometric and π -electronic structure that distinguish them from H₂P of close structure.

1. Due to the absence of the carbon atom in one of the *meso*-positions of the macrocycle in H₃Cor, a direct bond is formed that connects C _{α} – C _{α} -positions of the neighboring pyrrole fragments. This results in a contraction of the coordination cavity (CC). The result is a reduced size and trapezoidal shape of the CC. Thus, if in the case of H₂P the average diameter of the coordination cavity is 2.91 Å, the shortest distance between the intracyclic nitrogen atoms in the H₃Cor molecule is 2.53 Å [18]. Contracting CC has a number of consequences:

- ***π -electron-rich macrocycle of corroles.*** The number of π -electrons in the aromatic contour is the same for porphyrins and corroles, but the latter are distributed between a smaller number of sp²-hybrid atoms [18, 41]. At the same time, due to the reduction of symmetry of the macrocycle (in the case of free ligand) from D_{2h} in porphyrins to C_s in corroles, π -electronic density in the molecules of the latter is distributed unevenly, and C _{α} -C _{α} -bipyrrole fragment of the molecule is usually more electron-rich in comparison with dipyrromethane fragment, which leads to the appearance of a significant dipole moment [18, 26]. In turn, the non-uniformity of π -link indicates some decrease in the aromaticity of the macrocycle H₃Cor compared to H₂P [18, 33];

- ***three anions in the macrocycle of corroles with a coordination cavity of composition N₄H₃.*** This atomic composition of the coordination cavity, which is necessary to preserve the aromaticity of the molecule, contributes to the stabilization of higher degrees of oxidation of metals in the composition of complexes of corroles compared to the porphyrins with a two-anion coordination center [19, 24, 26-28, 30, 25, 42]. Currently, Mn^{IV} and Mn^V [28, 33, 43-46], Fe^{III}, Fe^{IV} and Fe^V [19, 27, 42, 43, 47-52], Co^{IV} [36, 53-56], Ni^{III} [18, 27, 57], Cu^{III} [57-62], Ag^{III} [63, 64], Au^{III} [65] etc. corrole complexes are discovered. In cases when the degree of metal oxidation in the complex is not stable, it is possible to transfer an electron intramolecularly from the macrocyclic π - system to *d*-orbital of a metal – this is how the so-called non-innocence of the corrole ligand is realized, i.e., corroles are redox-active ligands [26, 27, 40, 43, 57, 60, 66];

- ***N-NH-tautomerism is much easier*** [14].

It is caused by spatial convergence of intracyclic aza- and imino-centers in the corrole molecule. If in the case of H₂P, the energy barrier between the pair of the most stable tautomers is about 17 kcal/mol, in the case of H₃Cor, the same value does not exceed 2.45 kcal/mol [30]. Recently it has been shown that corroles are actually always mixtures of spectrally distinguishable N-NH tautomers (Fig. 2) whose ratio depends on temperature [67–71]. Since it has become known that the electronic and geometric structure of corrole tautomers, and hence their reactivity, is significantly different, most of the quantitative characteristics describing the reactivity of these compounds should only be assumed [26, 32, 68].

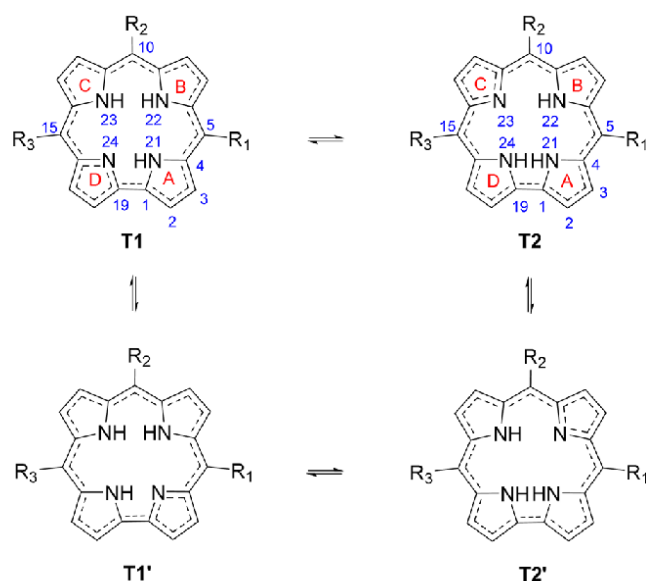


Fig. 2. NH-Tautomerism of free-base *meso*-substituted corroles [71]

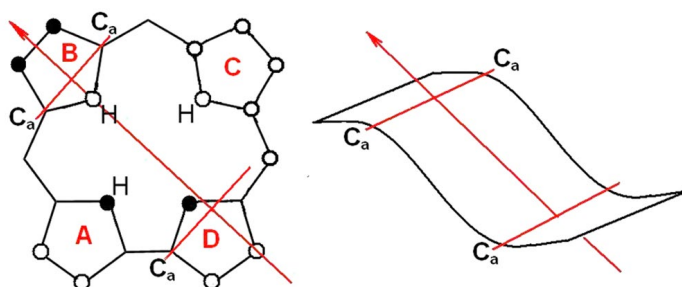
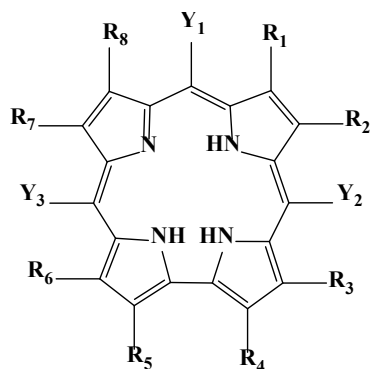


Fig. 3. «Wave-like» distortion of the corrole macrocycle [71]

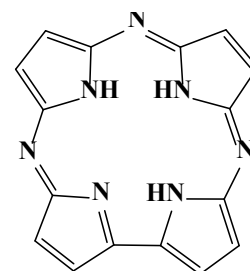
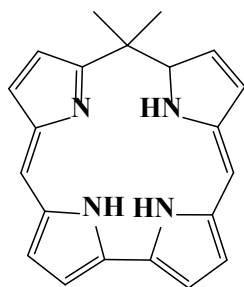
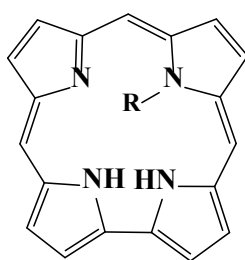
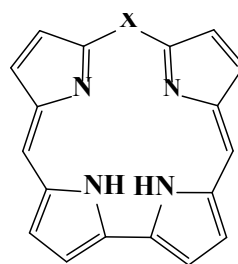
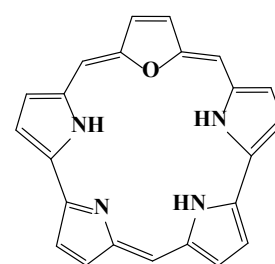
on the one hand – compression of the coordination cavity of the macrocycle, on the other – facilitation of formation of hydrogen intramolecular NH-N bonds [14, 71]. The first of these factors destabilizes the planar structure of the corrole macrocycle, while the second, on the contrary, promotes it. As a result, molecules of free ligands of *meso*-substituted H_3Cor have "wave-like" distortion of the macrocycle [71] (Fig. 3).

Like porphyrins, corroles can be conventionally divided by the type of outwardly cyclic substitution into β - (mol. 4-5), *meso*- (mol. 6-10) and repeatedly (*deca*-, *undeca*-) substituted molecules, e.g. compound 11 [29]. They can also be categorized by the nature of structural similarity with other classes of H_2P and porphyrinoids – corrolazines 12 (a combination of elements of structures of a corrole and a porphyrazine) [42], triazatetrabenzocorroles (a combination of elements of structures of a corrole and a phthalocyanine) [74, 75], isocorroles 13 (a combination of elements of structures of a corrole and a phlorine) [76, 77], N-substituted corroles 14 [78], heteroatom-substituted corroles, while the atoms of carbon or nitrogen can be substituted both externally (depending on their *meso*- position) and intracyclically, respectively, by different heteroatoms (O, S, Se) 15 [19], inverted corroles [79], extended coordination cavity corroles 16 [80, 81], etc.

2. For metal complexes of corroles, in spite of compression of the π -system and redistribution of electronic density in it, it is mainly a flat structure, weakly dependent on the type of peripheral substitution [19, 27, 32]. Only molecules of corrole complexes with copper(III) are strongly saddle-like and non-flat [27, 58, 66], and corrugation is not typical for corroles at all [30, 72]. In addition to complex formation, the protonation of H_3Cor molecules leads to saddle-shaped distortion of their structure, which is typical for protonated forms H_2P [18, 73]. However, even in the case of free ligands of *meso*- substituted corroles, there are deviations of molecules from planarity, which is the result of two opposite trends:



- 4** $R_{1-8}=\text{Et}$, $Y_{1-3}=\text{H}$;
5 $R_1=R_8=\text{Et}$, $R_{2-7}=\text{Me}$, $Y_{1-3}=\text{H}$
6 $R_{1-8}=\text{H}$, $Y_{1-3}=\text{C}_6\text{F}_5$
7 $R_{1-8}=\text{H}$, $Y_{1-3}=\text{Ph}$;
8 $R_{1-8}=\text{H}$, $Y_{1-3}=4\text{-NO}_2\text{Ph}$;
9 $R_{1-8}=\text{H}$, $Y_{1-3}=4\text{-MeOPh}$;
10 $R_{1-8}=\text{H}$, $Y_{1-3}=4\text{-Py}$
11 $R_{1-8}=\text{Br}$, $Y_{1-3}=\text{Ph}$

**12****13****14****15** (X=O, S, Se)**16**

Synthetic approaches to obtaining, functionalization and post-functionalization of corroles

Synthesis of β -substituted corroles. As mentioned above, the development of corrole chemistry can be divided into two major stages. The first one started in the '60s of the XX century and is related to the synthesis and investigation of the properties of β -substituted corroles; the second one started in the late '90s of the XX century and is marked by the synthesis of *meso*-substituted heterocyclic macrocycles. Interestingly, the second stage proved to be more productive than the first one, which was greatly facilitated by the high synthetic availability of *meso*-substituted H_3Cor as compared to β -substituted compounds of this class [29]. While pyrrole or dipyrrolymethanes and aromatic aldehydes are the initial substances for the synthesis of *meso*-substituted corroles, the synthesis of β -substituted corroles usually requires substituted pyrroles of rather complex structure, as well as bi-, tri- and tetrapyrrole precursors, the preliminary synthesis of which itself is laborious. In addition, when obtaining β -substituted macrocycles, the product is often not a free ligand, but a metal complex, since the initiator of the process of their assembly is cobalt acetate(II). However, if in the case of H_2P it is not difficult to remove the metal from the complex, this problem is nontrivial in the case of corroles, because not all metallo-corroles form a free ligand when trying to demetallize [82]. Obviously, these very reasons resulted in a low degree of study of β -substituted corroles.

Since β -substituted compounds are much more difficult to access than *meso*-substituted compounds, let us only briefly consider the methods of their synthesis. The main methods for obtaining β -substituted corroles described in the literature are:

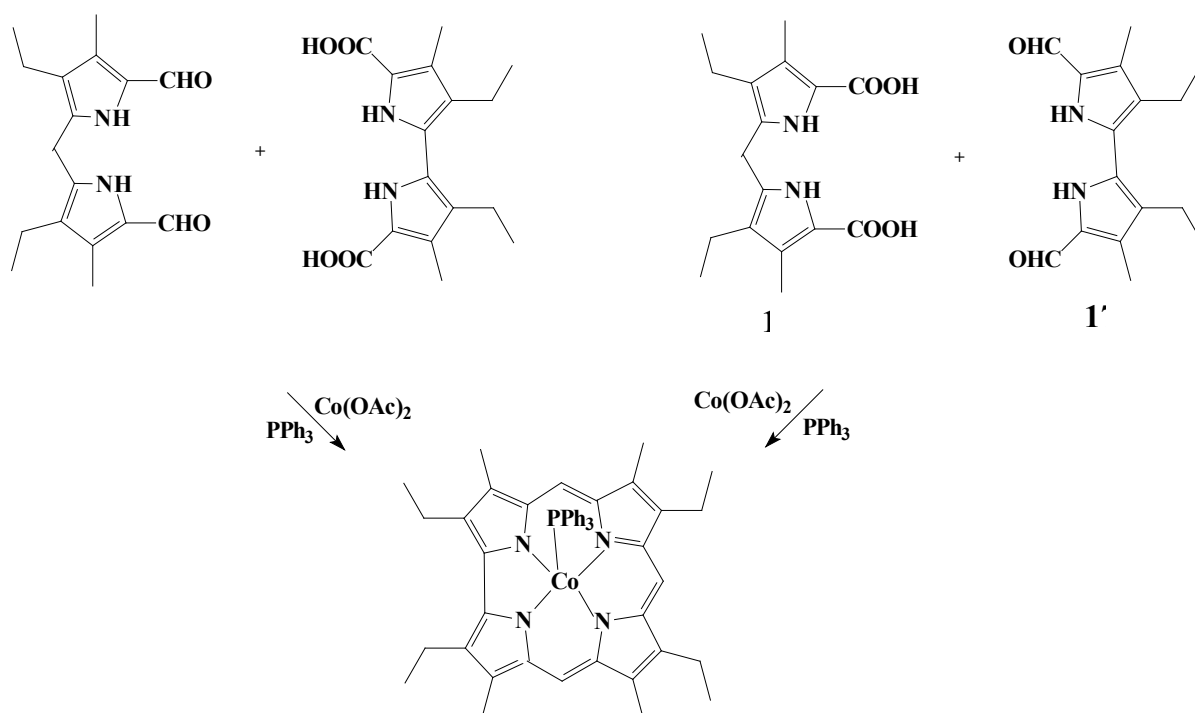
- oxidative cyclization of biladienes-*a,c*;
- [2+2]-cyclization or condensation of dipyrrolymethanes with α,α -bipyrroles;
- tetramerization of α -substituted pyrroles;



- extrusion of the thiaphlorin macrocycle.

Historically, the first and most common way of synthesis is cyclization of biladienes-*a,c* [35]. This method is suitable not only for obtaining β -substituted corroles, but also for asymmetrical mixed-type substitution compounds with substituents both in β - and in *meso*- macrocycle positions. The cyclization process is done in methanol containing basic reagents (ammonia, sodium acetate) – either under the light [35] or in the presence of oxidizing agents such as potassium hexacyanoferrate (III) or benzoyl peroxide [83]. The yield of corrole at this stage is 20–60%. The intermediate product in the process is bilatriene, which is cyclized to form a corrole. β -Substituted corroles can also be synthesized from 1,19-dihalogenobiladienes-*a,c* [84–88].

The methods associated with the condensation of pyrroles and bipyrroles are complicated by the fact that the formation of the corrole macrocycle occurs only in the presence of Co^{2+} ion, and the reaction product is not a free ligand of corrole, but its complex with cobalt [89]. Thus, the authors [89] obtained corrole by utilizing the [2+2]-condensation method at the interaction of 5,5'-diformyl-2,2'-dipyrrolylmethane **17** with 2,2'-bipyrrole-5,5'-dicarboxylic acid **18** in an acidic medium in the presence of cobalt acetate (II) and triphenylphosphine. The same result was observed when **19** and **20** compounds were used as source substances [18]:

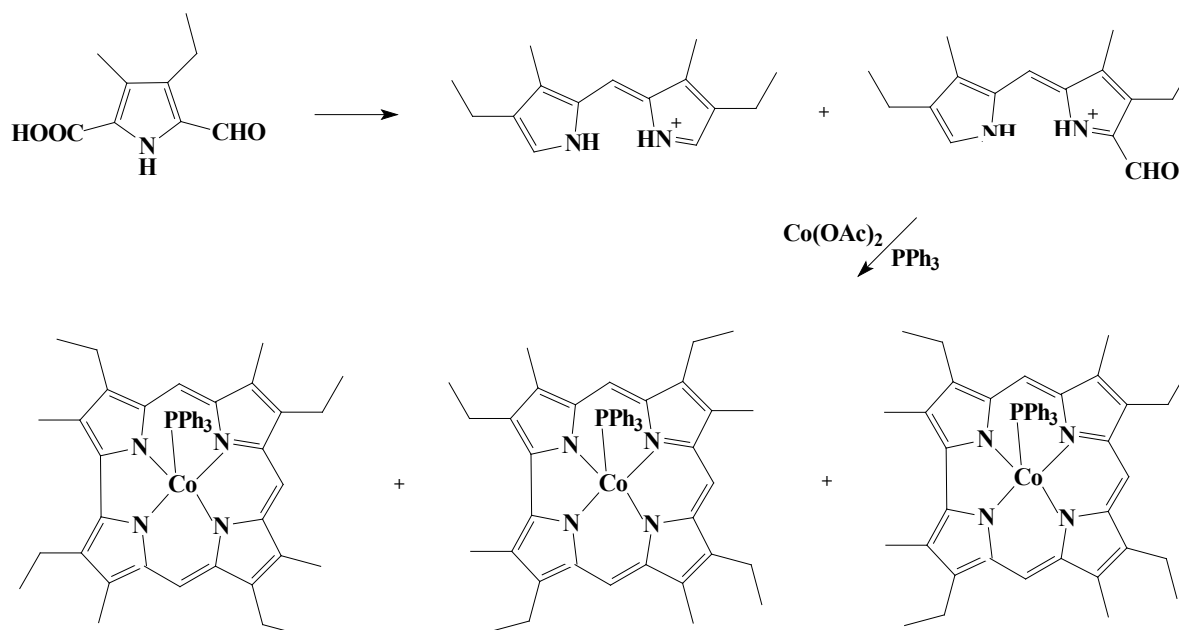


In the absence of Co^{2+} ion, no formation of macrocycle corrole was observed [90]. Presumably, the Co^{2+} ion is needed to stabilize the intermediate tetrapyrrole product, as well as the *template center* for direct construction of the corrole macrocycle. At the moment, there is no information about the possibility of obtaining free ligands of corroles from their complexes with cobalt in other scientific sources. Thus, the method is limited only to obtaining complexes of β -substituted corroles with cobalt when free ligands cannot be isolated.

The same can be said about the method of tetramerization of α -substituted pyrroles, the initial substances for which are the derivatives of 2-(α -hydroxybenzyl)pyrrole or 2-formylpyrrole. The process is carried out in ethanol medium in the presence of strong acids.



As in the previous case, the catalyst for the formation of the macrocycle corrole is a Co^{2+} ion, usually in the form of cobalt(II) acetate in the presence of triphenylphosphine. When β -substituted 2-(α -hydroxybenzyl) pyrroles are used, *undeca*-substituted corroles are obtained in the form of complexes with cobalt [18, 29]. Under these conditions, a mixture of three isomeric complexes containing a macrocycle of corrole and the ethioporphyrin I complex [18] is formed from the derivatives of 2-formylpyrrole, which can be separated to components by chromatography:



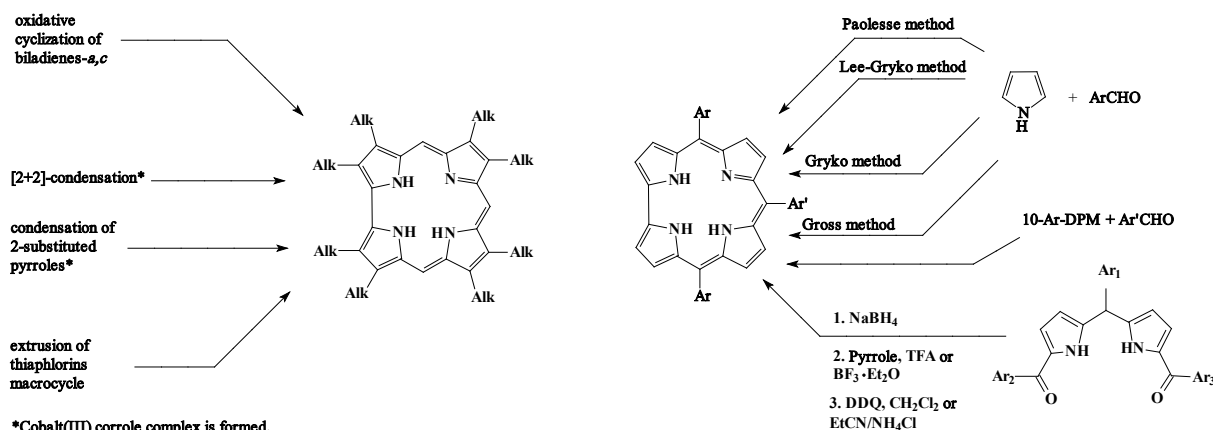
It has been found that the intermediate products in the synthesis are the corresponding dipyrromethanes [84].

The method of production from thiaphlorins is associated with laborious synthesis of initial compounds and their low stability [91]. It is known that boiling *meso*-thiaphlorins in *o*-dichlorobenzene for 2 hours leads to corroles with an output of about 40% [91]. The presence of triphenylphosphine in the reaction mixture increases the corrole yield up to 60%, but no explanation for this experimental fact has been found.

Synthesis of meso-substituted corroles. The methods of synthesis and further functionalization of *meso*-substituted corroles should be described in more detail.

The first reports on the synthesis of *meso*-substituted corroles without substituents in β - macrocycle were published almost simultaneously by two scientific groups independently of each other in 1999. The first representatives of this class of compounds were 5,10,15-tris(pentafluorophenyl)corrole **6** (Z. Gross, Israel, [38]) and 5,10,15-triphenylcorrole **7** (R. Paolesse, Italy, [39]) [33]. Later on, the methods for the synthesis of *meso*-substituted corroles were improved and refined by other authors, of which the works of the D. Gryko group (Poland) should be particularly noted.

The overwhelming majority of methods for obtaining *meso*-substituted corroles are based on condensation reactions of pyrrole or 10-aryldipyrrolylmethane with aromatic aldehydes:



But the key aspects are the synthesis conditions, as well as the structure of the target product. Depending on the nature of aryl *meso*-substituents, the same synthesis method may produce very different outputs of the compounds. In addition, the synthesis of *meso*-substituted H₃Cor is complicated by the formation of a significant number of by-products, one of which is usually *meso*-substituted porphyrin (H₂P). The chromatographic separation of the mixture H₃Cor and H₂P is quite time consuming because the compounds have very close retention times (R_f). Therefore, often the main task in the synthesis of *meso*-substituted corroles is to minimize the competitive formation of porphyrin and other by-products. It is this circumstance that explains the large influence of seemingly not too significant synthetic parts, such as the ratio and concentration of reagents, the nature of the solvent, the process duration, etc., on the final result of the synthesis, as well as relatively low yield of corroles (up to 20–30%, higher yield is very rare). Thus, it would not be a big exaggeration to say that the synthesis conditions for each specific H₃Cor should be selected individually.

Symmetrical corroles of A₃B-type (containing three identical substituents in *meso*-molecule) are usually obtained by condensation of pyrrole with aromatic aldehydes. Essentially, this method is a modified Rotmund reaction [92], widely used for the synthesis of *meso*-substituted porphyrins. There are several variations of the considered method, and different modifications of the synthesis are better suited to one group of compounds and less applicable to another.

Paolesse method. One of the synthesis variations consists of boiling a mixture of pyrrole and aromatic aldehyde in acetic acid for 3–4 hours in a molar ratio of 3:1 [93]. With large amounts of aldehyde in the reaction mixture, the formation of the corresponding *meso*-tetraarylporphyrin comes first. However, when there is a large excess of pyrrole, resinous polycondensation products are formed, which makes it very difficult to clean the target product and significantly decreases its yield. Depending on the nature of the substituents, the corrole yield varies between 4 and 22%; the highest corrole yield is obtained by using aldehydes containing electron acceptor substituents in the aroma ring. 2,6-disubstituted benzaldehydes do not react, which seems to be due to steric difficulties [93].

Lee-Gryko method. The authors [94] proposed a technique for the synthesis of *meso*-substituted corroles based on the interaction of pyrrole and aldehyde catalyzed by trifluoroacetic acid (TFA), and the subsequent oxidation of the formed at the first stage of a linear tetrapyrrole product (bilane) to corrole by dichlorodicyano-*p*-benzoquinone (DDQ). According to the



original description, this method requires relatively laborious cleaning of intermediate products (bilanes), as well as the use of hard-to-reach and toxic solvent - propionitrile.

The authors of [95] improved the technique [94] and showed that propionitrile can be successfully replaced with dichloromethane. The details of the process depend on the reactivity of aldehyde. In the case of reactive aldehydes containing electron-acceptor substituents, the duration of the first stage of the process is 10 minutes, and the molar ratio of pyrrole to aldehyde is 1.5:1. The molar TFA-aldehyde ratio in this case is 0.012:1. Molar ratio of pyrrole-aldehyde 3:1 was used for the process with medium chemically active aldehydes, the first stage was processed within 1 hour. In addition, a higher concentration of trifluoroacetic acid (molar ratio acid - aldehyde 0.023:1) was used. Corrole yield was 8–15%. To obtain corroles from sterically hindered aldehydes, the time of the first stage of the process was significantly increased (up to 16 hours), an excess of pyrrole in relation to aldehyde (molar ratio – 5:1) was used, as well as an increased concentration of trifluoroacetic acid (molar ratio acid – aldehyde 0.21:1) at the first stage. Thus, in particular, 5,10,15-tris-(2,6-dichlorophenyl)-corrole with yield of 9% was obtained and for the first time *meso*-trimesitylcorrole with yield of 7% was obtained.

The second stage of the process was conducted identically for all types of compounds and also included evaporation of the solvent, dissolution of the residue in dichloromethane, and addition of DDQ solution in dichloromethane for oxidative cyclization.

Gryko method. The authors [96] proposed the following conditions for the synthesis of *meso*-substituted corroles: reaction medium – aqueous solution of methanol (1:1 volume), catalyst of the first stage of the process – hydrochloric acid, time of the first stage of the process – 3 hours, molar ratio of pyrrole – aldehyde - 2:1. The resulting intermediate product, bilane, is deposited under these conditions in a sludge which is extracted by chloroform and oxidative cyclization is performed with DDQ or *para*-chloranil by boiling; the second stage duration is one hour. With this method, the authors [96] managed to achieve sufficiently high corrole yields – more than 30%. The advantages of the method are also its simplicity, accessibility, and relatively mild synthesis conditions. However, 5,10,15-tris(pentafluorophenyl)corrole **6** is formed only in trace amounts when trying to obtain using this method, and 5,10,15-tris(4-pyridyl)corrole **10** is not formed at all.

Gross Method in the absence of solvent. Highly electron-deficient aldehydes (fluorinated benzaldehyde: pentafluorobenzaldehyde, 2,6-difluorobenzaldehyde, as well as heptafluorobutanal) can enter into a condensation reaction with pyrrole in the absence of solvent, on a solid substrate (aluminum oxide) [38] heated to 100°C for 4 hours with subsequent washing out of the reaction mixture from the substrate and oxidation of DDQ. The ratio of aldehyde to pyrrole is equimolar, or pyrrole is taken in some excess (up to twofold). 5,10,15-Tris(pentafluorophenyl)corrole **6** is formed when using this method with a yield of about 11%, 5,10,15-Tris(2,6-difluorophenyl)corrole - with a yield of about 6% [38]. Chlorinated derivatives of benzaldehyde either do not react or give only very low yields of the product (1% - in the case of 2,6-dichlorobenzaldehyde with twofold molar excess of pyrrole); under these conditions, the unsubstituted benzaldehyde forms only 5,10,15,20-tetraphenylporphine (with 5-8% yield) [38].

Corroles of A₂B type (with the same substituents in positions 5 and 15 of the macrocycle and the other substituent in position 10) are obtained by condensation of



10-aryldipyrrolylmethane with aromatic aldehydes [95-97]. The reaction conditions are almost identical to those of pyrrole condensation with aldehydes according to Lee-Gryko (in dichloromethane or chloroform in the presence of trifluoroacetic acid) and Gryko (in the water-methanol system in the presence of hydrochloric acid). Thus, during the process according to the Lee-Gryko method, it was shown that the highest corrole yields are achieved with small additions of acid (0.02 of aldehyde substance), molar ratio of dipyrrolylmethane-aldehyde 2:1; the optimal time for the first stage of the process is 5 hours. The second stage – oxidative cyclization of the intermediate product – was conducted using DDQ as an oxidant. Corrole yield – from 6% to 30% with minimum yield of the corresponding porphyrin.

ABC-type corroles is also known (all three substituents in *meso* positions of macrocycle are different). The main method of their production is the condensation of dipyrrolylmetandicarbinols with pyrrole (see the above scheme) with subsequent oxidation of DDQ [98-100]. Instead of pyrrole, 2,2'-bipyrrole can be used [101]. Sometimes such compounds can be obtained from A₂B-corroles by modifying one of the *meso*-substitutes [102].

Corroles with mixed type of substitution (having substituents both in β - and in *meso*-positions of a molecule) are obtained either by using source substances of necessary structure (*meso*-phenyl-substituted biladienes or β,β -disubstituted pyrroles) or by modification of an already existing macrocycle.

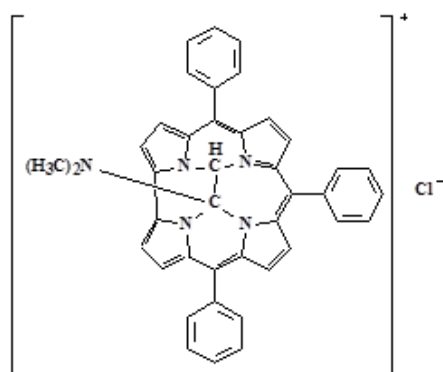
Features of corrole functionalization

The methods of modification (or, as they say, functionalization) of the corrole macrocycle should be discussed in more detail, since they demonstrate not only synthetic approaches and capabilities as such, but also give an idea of the diversity and peculiarities of the corrole chemistry in general. If β -octaalkylcorroles, due to their macrocyclic propensity to open, are characterized only by some types of electrophilic substitution reactions (alkylation and acylation on the intracyclic nitrogen atoms, formylation – on the *meso*-position with the formation of non-aromatic derivatives, see below), the range of similar *meso*-triarylcorrole reactions is much wider and includes halogenation, nitration, chlorosulphonation, carboxylation, etc. in addition to the mentioned processes [29, 33]. Some of the noted reactions may lead to the formation of products of unusual structure that have no analogues in the porphyrinic series, which once again emphasizes the uniqueness of the reactivity of corroles.

Alkylation of β -substituted corroles by methyl iodide in acetone in the presence of potassium carbonate leads to the formation of a mixture of isomeric N-monomethyl-corroles [35]. N,N'-dialkylcorroles can be obtained by alkylation of N-substituted corroles or N-alkylcorroles under severe conditions, e.g. from unsubstituted corrole and CH₃I when heated in a sealed tube (100°C) for 15 hours [18]. Alkylation of *meso*-substituted corroles by different agents (benzylbromide, 2-chloromethylpyridine, ethylbromacetate) also leads to a mixture of N-monoalkylcorroles with the predominant formation of 21-N-alkylcorroles. 21,22-N,N'-dialkyl-derivatives of *meso*-triarylcorrols can be obtained by treating H₃Cor free-bases with methyl iodide in boiling acetone in the presence of potassium carbonate [103].



Acylation of β -octaalkylcorroles with acetic anhydride leads to formation of 21-N-acetyl derivatives [18, 104]. Attempts to form β -substituted corroles with Vilsmeier reagent (mixture of N,N-dimethylformamide and phosphorus-trichloride oxide POCl_3) produce non-aromatic *meso*-dimethylaminomethyl-derivatives with distorted macrocycle, but the interaction of these derivatives with cobalt(II) acetate in the presence of triphenylphosphine leads to the splitting of

**21**

dimethylaminomethyl group, rearomatization of macrocycle and the formation of complex β -octaalkyl-*meso*-formylcorrole with cobalt [18]. Zinc acetate does not cause such transformations

[105]. Vilsmeier treatment of 5,10,15-tris(pentafluorophenyl)corrole (as a complex with gallium) at a lower temperature (about 0°C) leads, depending on the ratio of reagents, to 3-monoformyl- or 3,17-diformyl derivative [106]. 5,10,15-Triphenylcorrole (in the free-base form) under similar conditions forms a mixture of 3-monoformyl-derivatives and a product with an unusual structure **21**,

which has no analogues in the porphyrinic series and is formed by the interaction of Vilsmeier reagent with the nitrogen atoms of the coordination cavity of corrole [107].

Carboxylation of meso-substituted corroles is possible in two ways [108, 109]. 5,10,15-tris(pentafluorophenyl)-corrole **6** as an example shows [108] that the treatment of its gallium complex with phosgene in toluene leads to the formation of 3-carboxy-derivatives. The impact of phosgene on the free ligand under similar conditions leads to the formation of 21-N-COCl-substituted corrole [108]. Another method of carboxylation is mild oxidation of the formyl group in a macrocycle (5,10,15-triphenylcorrole-3-carbaldehyde, for example) with hydroxylamine in a carefully dried acetonitrile (MeCN) in the presence of phthalic anhydride, and both corrole free-base and copper complex can be involved in the reaction [109]. At the same time, it is known that standard methods of aldehyde (formyl) group oxidation do not yield results with respect to heterocyclic macrocycle compounds [108], and the use of strong oxidizing agents such as KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ leads to the formation of complex mixtures of oxidation products, which is also typical for formylporphyrins [109].

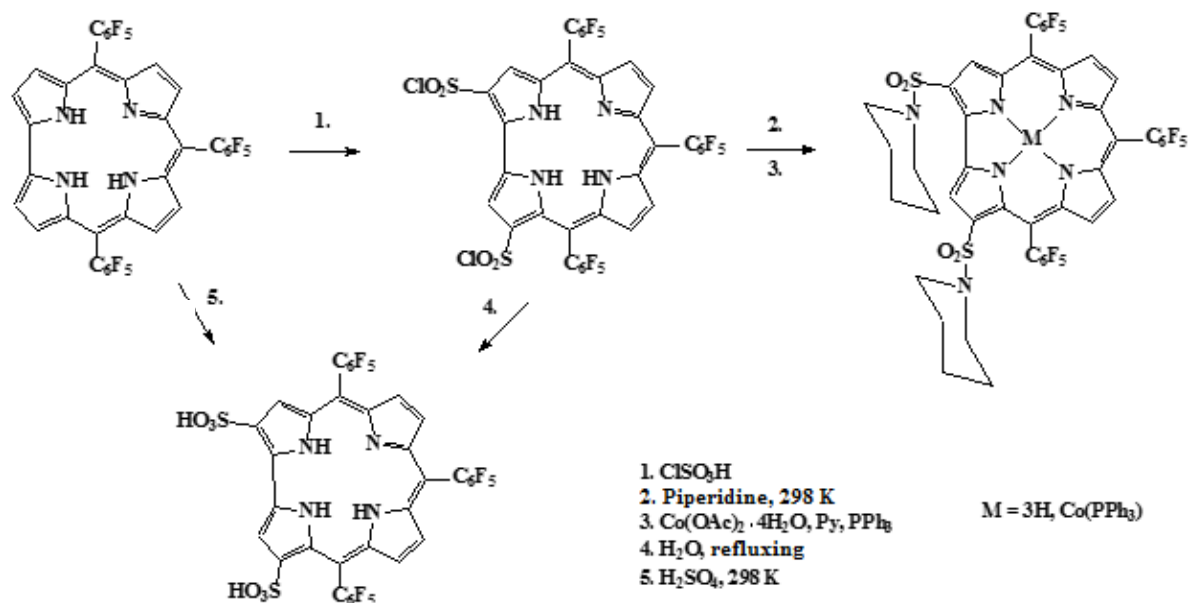
For *nitration* of corroles, in most cases milder conditions are required than for nitration of porphyrins, because classical nitrating agents ($\text{HNO}_3/\text{H}_2\text{SO}_4$, N_2O_4 , AgNO_2/I_2) used in the reaction to porphyrins, in the case of corroles, are ineffective and can lead to macrocycle destruction and the formation of a mixture of polynitro-compounds. Thus, the authors [106] conducted the nitration of 5,10,15-tris(pentafluorophenyl)corrole (in the form of gallium complex) after corrole was exposed to sodium nitrite in acetonitrile with subsequent addition of hexachloroantimonate tris(4-bromophenyl)amine in the reaction mixture. The main product is a 3-mononitro-derivative (yield is about 84%), but a 3,17-dinitro-derivative also forms (yield is about 8.9%). An increase in the content of hexachloroantimonate tris(4-bromophenyl)amine in the reaction mixture leads to a predominant formation of 3,17-dinitro- and 3,17,18-trinitro-derivatives, although the yield of the latter still does not exceed 27% [106].



Corrole nitration can also be carried out when the free ligand (a complex of 3-nitrocorrole with silver is formed) is exposed to silver nitrite in DMF [110], as well as silver nitrite and iodine, although the latter method is suitable only for corroles containing electron-donor substituents which favor the reaction, while electron-deficient heterocyclic macrocycles in these conditions are destroyed with the opening of the macrocycle [29]. Further studies of the reaction in the corrole-AgNO₂-NaNO₂ system showed that the ratio of mono- and dinitro-derivatives of 5,10,15-tris(4-tolyl)corrole is determined by changing the stoichiometric composition of the reagents [111]. The authors of [111] found that the nitro-substitution has a very significant effect on the spectral and redox properties of corroles, which is associated with a high degree of conjugation of the nitro-groups with the π -system of a macroring. 5,10,15-triphenylcorrole **7** in the form of a complex with gallium can be permeated with a mixture of LiNO₃/Ac₂O/HOAc in dichloromethane to 3-mononitro-derivatives; the use of NaNO₃ instead of LiNO₃ leads to a mixture of 3-mono and 3,17-dinitro-derivatives [29]. The paper [112] describes the production of β -trinitro-substituted corroles in the form of complexes with copper from free ligands with simultaneous complexation and nitration by a mixture of silver and sodium nitrite. In [113], the authors obtained β -tetranitro-derivatives of corroles in the form of complexes with cobalt when exposed to sodium nitrite and trifluoroacetic acid. The introduction of cobalt was necessary to convert initially formed isocorroles into corrole complexes [113]. The use of a two-phase system of dichloromethane – an aqueous solution of sodium nitrite and HCl – leads to the formation of a mixture of 3-mononitro-derivatives and 3-nitro-5-*iso*-corrole, which is not re-aromatized when exposed to cobalt salts, as well as the original compound [113].

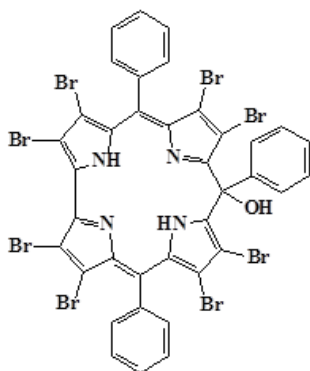
The complexes of *meso*-substituted corroles of various structures with iron(III) [114], germanium(IV) [115] and phosphorus(V) [116] were also subjected to nitration.

The reaction of chlorosulphonation of corroles was studied using 5,10,15-tris(pentafluorophenyl)corrole **6** as an example [106]. When the corrole-ligand is exposed to chlorosulfonic acid, 2,17-bis(SO₂Cl)-derivative is formed with yield close to 100%. Boiling this compound with water for 12 hours produces a corresponding 2,17-disulfonic acid with 71% yield. The amount of 3,17-isomers does not exceed 3-4% [106]:





If *meso*-tris(2,6-difluorophenyl)corrole is used as a starting material, the selectivity of the process is significantly reduced.



22

Sulfonation of 5,10,15-tris(pentafluorophenyl)corrole **6** with concentrated sulfuric acid at room temperature gives quantitative yield of mixture of 2,17- and 3,17-isomeric disulfonic acids in 9:1 ratio [33, 117]. The reaction of 5,10,15-triphenylcorrole **7** with chlorosulfonic acid selectively produces 2-sulfo-derivative [118]. The selectivity of chlorosulfonation of phosphorus(V) corroles is discussed in [119].

Halogenation. Among the reactions of halogenation, *bromination* of corroles is used most often [29, 33]. In [58], the method of bromination of corrole complexes with free bromine has been proposed. The process is conducted using copper complexes of *meso*-triarylcorroles in chloroform medium with the following addition of pyridine at room temperature. The complexes of the corresponding β -octabrom-*meso*-triarylcorroles are thus obtained. Free ligands can be obtained from them when exposed to sulfuric acid [33, 82], although the process is complicated by the formation of by-products (so-called isocorroles – compounds with a broken conjugation circuit, different from the corroles themselves by the presence of OH-group in one of the *meso*-positions of the macrocycle, for example, comp. **22**) as well as process reversibility. Octabromoproducts are obtained by bromination with excess bromine in methanol of iridium complex of 5,10,15-tris(pentafluorophenyl)corrole **6** [120], and also complexes of this corrole with other metals (Fe, Co, Mn) [121]. At attempts of bromination of free-base of 5,10,15-triphenylcorrole **7** with N-bromosuccinimide (NBS), the corresponding isocorrole – compound **22** is obtained [122]. Free bases of β -octabromo-*meso*-triarylcorroles (e.g. comp. **11**) can be obtained by demetallation of the corresponding copper complexes [122, 123]. The literature also describes a number of examples of partial bromination in corrole molecules and their metal complexes [33]. For example, in [124], as a result of the reaction of 5,10,15-tris(4-tolyl)corrole with HBr in acetic acid with subsequent addition of DDQ, a mixture of mono-derivatives (2-bromo- and 3-bromo-) was obtained with yield of about 15% each. At chlorination of the same corrole in the presence of HCl, we obtained 3-chloro- (43%) and 3,17-dichloro- (9%) derivatives. The results of the bromination of corrole complexes with different metals using NBS differ significantly among themselves. Thus, if the product in the case of silver complexes is 2,17-dibromosubstituted complex [125], then in the case of complexes Cr(V), Ga(III), and Al(III) – β -octa-substituted compounds [33].

Iodination of complexes of 5,10,15-tris(pentafluorophenyl)corrole **6** with aluminum and gallium by N-iodosuccinimide leads to the formation of 2,3,17,18-tetraiodosubstituted, and when exposed to iodine – 2,3,17-trisubstituted product [126, 127].

By chlorination of the complex of the same corrole with cobalt(III) with free chlorine in benzene with subsequent exposure to NaBH₄ β -octachlorosubstituted derivative (90%) was obtained [128]. Authors of [129] also conducted β -chlorination of complexes of *meso*-pyrimidinylcorroles with copper by means of N-chlorosuccinimide with 46% yield with subsequent demetallation of the complex in the presence of the reducing agent [130]. Interesting results



were obtained at *meso*-chlorination of isomeric 5,10- and 5,15-bis(pentafluorophenyl)corroles with the reagent Palau'Chlor (2-chloro-1,3-bis(methoxycarbonyl)guanidine) in chloroform medium at room temperature [131]. At the same time, while 10-chlorine-derivative was obtained with 88% yield, 5-chlorine isomer was obtained only in trace amounts, which the authors attribute to high reactivity of the latter in oligomerization processes. Chlorination of cobalt and gallium complexes under similar conditions gives complex and difficult to separate product mixtures [33].

β -octafluoro-*meso*-triarylcorroles are also described in the literature, but they are obtained by condensation of β,β -difluoropyrroles with aromatic aldehydes similar to β -unsubstituted triarylcorroles [132].

The presence of corroles of certain functional groups in molecules allows to modify them using the whole arsenal of synthetic organic chemistry to give the required practically useful properties. *Nucleophilic substitution reactions and metal-catalyzed reactions* can be mentioned in particular.

For 5,10,15-tris(pentafluorophenyl)corrole, 6 nucleophilic substitution reactions are part of their specific aspects. In these reactions, fluorine atoms enter into *para*-positions of phenyl rings [38]. Thus, this corrole when exposed to 2-pyridyllithium forms 5,10,15-tris(4-(2-pyridyl)-2,3,5,6-tetrafluorophenyl)corrole, the treatment of which with methyl iodide forms the corresponding pyridinium salt with water solubility of about 2 mg/ml. In this case, there are no observable phenomena of aggregation during salt dissolution, which was the motive for its use in the treatment of tumor diseases with photodynamic therapy (PDT). It was found that pentafluorophenyl fragments in positions 5- and 15- are more reactive, which was later used to develop a strategy for the synthesis of corroles [102].

It was later shown that in other corroles containing the pentafluorophenyl fragment, the fluorine atom in position 4 could be nucleophilically substituted for amines and amino acids (with a yield of 55-70%) [102, 133]. It was not possible to react with sterically hindered compounds such as diisopropylamine. The nucleophilic substitution of halogen in the corrole molecules carrying pentafluorophenyl fragments made it possible to conduct a whole range of reactions with different N-, O-, and S-nucleophiles and to obtain for the first time corrole conjugates with silicon nanoparticles, BODIPY fragments, galactose, chitosan, β -cyclodextrin, cholesterol, and other biologically active compounds [33]. Halogen substitution was also performed in the 2,6-dichloropyrimidine fragment [129]. The authors of [134, 135] found that nucleophilic substitution of hydrogen atoms is possible in β -positions of corrole molecules adjacent to the acceptor group (for example, nitro group). Thus, when 3-nitrocorrole in the form of a germanium or copper complex is exposed to 4-amino-1,2,4-triazole, the macrocycle is aminated, and 2-amino-3-nitrocorrole is formed. Another such example is the reaction of a 3-nitrocorrole copper complex with diethyl malonate, the result of which is the introduction of C-nucleophile into position 2 of the corrole macrocycle [134, 135].

The Suzuki-Miyaura cross-coupling reaction is also a nucleophilic substitution reaction in halogenated corroles and can occur both in β -positions and in the presence of halogen atoms in *meso*-substituents. The process is a nucleophilic substitution of halogen atoms associated with the aromatic nucleus with alkyl and aryl radicals when exposed to alkyl and arylboronic



acids in the presence of palladium-containing catalysts. In recent years, this reaction has played a major role in the chemistry of tetrapyrrole heterocyclic macrocycle compounds as a method that opens up broad synthetic possibilities for the creation of new structures. In fact, it is an alternative to traditional organometallic magnesium synthesis with Grignard reagent, which is ineffective in the case of macrocyclic halogen-substituted compounds. The authors of [136-138] demonstrated the applicability of the Suzuki-Miyaura reaction in relation to corroles as a method that allows to obtain undecaaryl-substituted derivatives.

When exposing the copper complex of β -octabromo-*meso*-triphenylcorrole **11** to 4-chlorophenylboronic acid in toluene in the presence of anhydrous potassium carbonate and palladium complex(0) as a catalyst, the authors [136] succeeded in obtaining the copper complex of β -octa(*p*-chlorophenyl)-*meso*-triphenylcorrole, demetallation of which leads to an isolation of a free ligand. The Suzuki-Miyaura reaction was conducted in an inert atmosphere (nitrogen) at 90°C for 4 hours; as a catalyst we used the compound [Pd(dmfu)(P-N)] (10% mol.), where dmfu is dimethylphumarate, and the designation P-N corresponds to the structure 2-(PPh₂)C₆H₄-1-CH=NC₆H₄-4-OMe.

In some cases, the Suzuki-Miyaura reaction does not run through all halogen atoms in the corrole molecule, and the unresponsive bromine is replaced by hydrogen [139]. In the literature, there are also examples of Suzuki-Miyaura reaction with the corroles partially brominated by β -positions [123, 138].

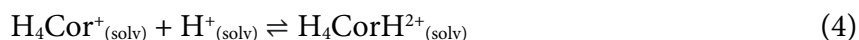
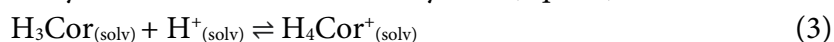
Main physical and chemical properties and reactivity of corrole macrocycles

As in the case of other tetrapyrrole heterocyclic macrocycle compounds, processes involving the coordination cavity of the macrocycle, namely, acid-base interactions and complex formation, are of particular importance in the case of corroles. Electronic absorption spectroscopy is a convenient tool for studying these processes, since, as will be shown below, different forms of corrole existence in solutions have sharply differing UV-Visible (UV-Vis) spectra. Therefore, it is convenient to consider the spectral characteristics of the corroles and its forms in the solutions together.

Acid-basic interactions of corroles. Corroles differ from H₂P in the number of NH-acid and N-base centers in the coordination cavity of the molecule. One of the three NH-protons is usually located outside the macrocycle plane, it is more spatially accessible and enters into the spectrally fixed acid-base interactions with electron-donor molecules (eq. 1, 2) [38, 39, 140-143].



N-based center in the corrole molecule, on the contrary, is the only one, so this heterocyclic macrocycle can attach the second extra proton only in environments with high acidity with localization of it to *meso*-carbon atom, forming a structure of isocorrole type; the second stage of protonation is accompanied by dearomatization of the π -system (eq. 3-4).





Acid-basic properties of corroles largely depend on position and electronic nature of substituents in macrocycle [26].

NH-acidity. A characteristic feature of corroles is its tendency to incomplete acid-basic interactions with solvents, in which the corrole can act as a donor (more often) (eq. 1-2), or an acceptor (eq. 3-4) of a proton. Acidic (protonodonor) properties of *meso*-substituted corroles are expressed more strongly than those of β -substituted compounds and much stronger than those of porphyrins of related structure, which is explained by an increase in the planarity of neutral molecule forms and a decrease in the distortion (and, consequently, spatial accessibility) of the coordination center. For this reason, *meso*-substituted corroles are particularly easy to start interacting as proton donors with electron-donor solvents. In this type of interactions, a sharply pronounced UV-Vis spectra change occurs (Fig. 4), which is usually interpreted in international papers as the formation of monoanion forms even in the absence of strong bases [39, 142, 143]. Corroles containing electron-donor substituents are most prone to interaction with electron-donor solvents [143]. Thus, according to [38], 5,10,15-tris(pentafluorophenyl)corrole **6** interacts similarly even with ethanol.

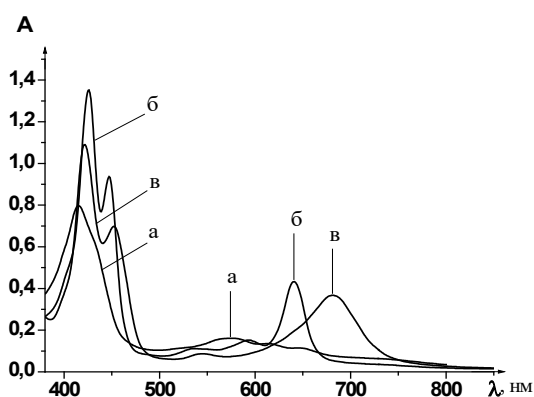


Fig. 4. UV-vis spectra of 5,10,15-triphenylcorrole **7** in dichloromethane (a), DMF (b), acetic acid (c) [39]

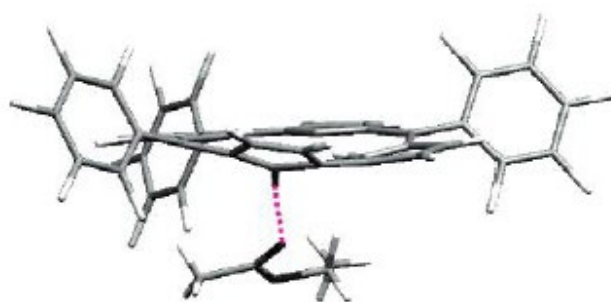


Fig. 5. X-ray crystallography data for 5,10,15-tris(pentafluorophenyl)corrole **6**, obtained from ethylacetate solution (dotted line shows H-bond with solvent molecule) [141]

The UV-Vis spectral features of corroles should be discussed in more detail here. UV-Vis spectra of β - and *meso*-substituted corroles are notably different from each other as well as from the UV-Vis spectra of the corresponding porphyrins [19, 144]. In addition, the nature of the solvent has a great influence on the type of UV-Vis spectra of *meso*-substituted corroles (Fig. 4) as well as the nature of the substituents in the macrocycle.

According to the authors [14, 57, 144, 145], in spite of significant visual difference between UV-Vis spectra of H₂P and H₃Cor, four-orbital Gouterman model (Fig. 6) suggested for porphyrins is good for interpreting corrole absorption spectra, but Q-absorption of H₃Cor (500-700 nm) is more complex than Q-absorption of H₂P. The orbital b_1 -HOMO of macrocycle of H₃Cor, as well as a_{2u} -HOMO of macrocycle H₂P (Fig. 6), holds a significant charge of *meso*-carbon atoms [57]; its change at *meso* substitution can affect the corresponding electronic transitions in the Q-band area.

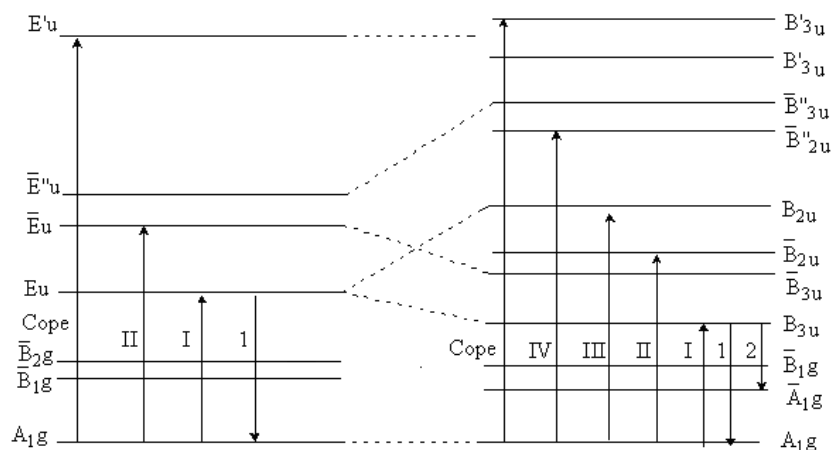


Fig. 6. Scheme of S-energetic levels of porphyrin macrocycle in H_2P (D_{2h}) and also in MP , H_4P^{2+} and P^{2-} (D_{4h}). Dash over symbol means vibrational satellite of electronic transition (and \downarrow - absorption and emission of quantum of UV or visible radiation by the molecule) [1]

Neutral forms of β -octaalkylcorroles are characterized by an intensive Soret band at 397–405 nm and less intensive absorption at 535–555 nm, as well as a band at 593–597 nm (Fig. 7).

Neutral forms of *meso*-substituted corroles are characterized by a Soret band at 413–430 nm, and three broadening bands of decreasing intensity with increasing wavelength (sometimes they merge as in 5,10,15-tris(4-nitrophenyl)corrole **8**, or degenerate into two, as in pentafluorophenyl derivatives) are at 570–660 nm (Fig. 7).

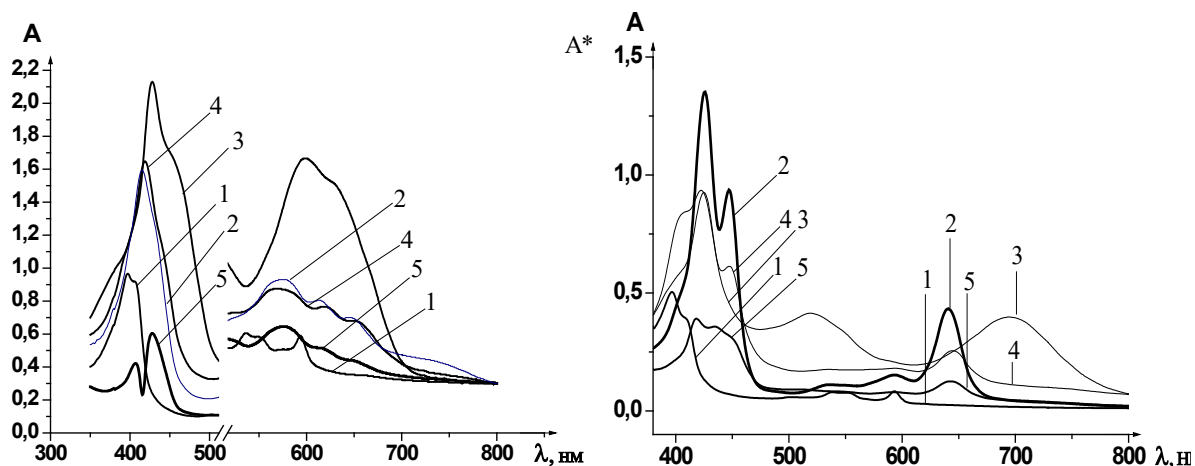


Рис. 7. UV-Vis spectra of free-base corroles in chloroform (left) and DMF (right): 1 - $H_3(\beta\text{-Me}_6\text{Et}_2)\text{Cor}$ **5**; 2 - $H_3(\text{ms-Ph})_3\text{Cor}$ **7**; 3 - $H_3(\text{ms-4-NO}_2\text{Ph})_3\text{Cor}$ **8**; 4 - $H_3(\text{ms-4-MeOPh})_3\text{Cor}$ **9**; 5 - $H_3(\text{ms-4-Py})_3\text{Cor}$ **10** [26]

In UV-Vis spectra of *meso*-substituted corroles in electron-donor solvents (pyridine [143], dimethylformamide [39]), the Soret band acquires a characteristic "split" appearance, and an intensive Q-band appears in the visible area (at around 620–650 nm, usually at 640 nm, Fig. 7), which is explained by acid-base interaction of macrocyclic compound with solvent. The degree of completeness of this type of interaction can be different and depends, on the one hand, on the nature of corrole (type of substitution and electronic nature of substituents), on the other hand, on the polarity and basicity of the medium. The authors of [39, 143] explain the change of UV-Vis spectra by the formation of anionic forms of corroles, but, in our opinion, there are grounds for a more "cautious" interpretation of these data due to the presence of incomplete



acid-base interaction with the formation of so-called incomplete proton transfer complexes, or H-associates [13, 140, 146, 147].

It should be noted that the cause of UV-Vis spectral changes of corroles depending on the nature of the solvent remains to be not fully researched. In [141] three possible causes of this phenomenon are considered. The first factor is NH-tautomerism of corroles, as tautomers are structurally different due to the reduced symmetry of the macrocycle. At the same time, tautomers have close deviations from planarity, close energies, and the proton exchange rate in them is quite high, so the authors [141] do not consider this factor as fundamental. The second factor is the possibility of deprotonation of the macrocycle in polar solvents, but there are doubts about the possibility of complete proton removal in the absence of a strong base. Finally, the third reason is the formation of hydrogen bonds involving NH-groups of corroles and solvent molecules. The authors of [141] have concluded from the data of X-ray structure analysis that the separation of 5,10,15-tris(pentafluorophenyl)corrole **6** from ethylacetate fixes the hydrogen bond between the NH-proton and the solvent molecule (Fig. 5). Similar conclusions were reached in [26, 140].

However, the authors of [68, 70, 71] hold a slightly different point of view and consider NH-tautomerism as the main cause of spectral changes in corroles in different media. In their opinion, tautomers have significantly different acid-base properties, and initially the more active one enters into specific interaction. If there are three types of particles in the solution at that moment, for example, a deprotonated form and two tautomers, this may explain the low sharpness (or even absence) of isobestic dots with corresponding titrations [70]. The authors of [70] failed to find correlations between spectral behavior of corroles in a solution and individual solvent parameters, so they concluded that it is necessary to consider a set of parameters, the main of which are basicity and polarity. This exact combination provides a way to explain the interaction between the corrole and a solvent, which correlates with the data from [26]. The authors of [70] also attempted to correlate the state of the corrole in the solution and the affinity of pyrrole (as a simplified model compound) to solvents in the formation of hydrogen bonds. No correlations were found, so the authors of [70] expressed doubts that the cause of spectral changes in corroles in different media is the formation of hydrogen bonds. The inconsistency is that in acetonitrile, the affinity of pyrrole fragments to which is lower, a corrole is in deprotonated form, while in dioxane, tetrahydrofuran and pyridine, the affinity of pyrrole fragments to which is higher, corrole is present in neutral form [70]. On the other hand, the properties of aromatic macrocyclic compounds are strongly influenced by the macrocyclic effect (MCE) [140], which is absent in the case of pyrrole, so the comparison of the properties of macrocycles and pyrrole should be approached with great care. In addition, even the corroles of different structures are very different in properties among themselves; the differences between corroles and porphyrins of close structure are even stronger, although all these compounds are based on the tetrapyrrole aromatic π -system. It is also possible that in the interaction of pyrrole with solvents, a fundamental role is played by one factor rather than two, as in the case of corroles. That is why there is no pronounced correlation for corroles. In any case, this issue is of great interest and requires further study. The authors of this review consider formation of corrole



compounds with hydrogen bonding (H-associates) with solvents in solutions as the main hypothesis.

β -octaalkylcorroles are the least prone to interaction with electron-donor solvents. Thus, 2,3,7,13,17,18-hexamethyl-8,12-diethyl-corrole ($H_3(\beta\text{-Me}_6\text{Et}_2)\text{Cor}$, **5**) exists as a neutral form even in a polar electron-donor solvent such as dimethylformamide (DMF) ($\text{DN}=26.6$; $\epsilon=36.7$). However, when this solution is stored for two weeks, neutral bands in the visible area of the UV-Vis spectra disappear while the Soret band is retained. The received solution, unlike initial corrole (violet-pink colour), possesses brownish colouring and the raised reactivity in complex formation reactions with metal salts. So, if the freshly prepared solution of compound **5** in DMF interacts with zinc acetate in a kinetic mode, then a long-stored solution of the same corrole forms a complex almost instantly, when mixing solutions, and UV-Vis spectra of reaction products in both cases are identical. The composition of this form of corrole has not yet been definitively clarified, although it seems that the interaction is of acid-base nature.

In solvents such as diethylamine and piperidine ($\text{DN}\geq 50$), UV-Vis spectra of corrole **5** is also subject to changes in Soret splitting and banding at around 570 nm (Figure 8). This type of UV-Vis spectra corresponds to the H-associated form of β -octaalkylcorroles. Monoanion is formed only in polar environments of high basicity, for example, in DMF – diethylamine (Et_2NH) mixture. In a mixture of acetonitrile (MeCN) – Et_2NH , the H-associate is formed first, but with time it turns into a monoanionic form. The latter is characterized by a split Soret band and two bands (576 and 595 nm) in the visible region (Fig. 8).

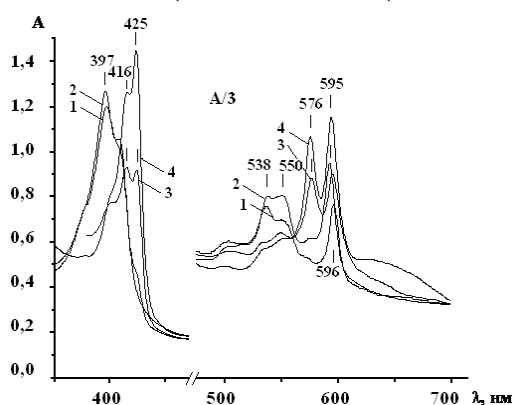


Fig. 8. UV-Vis spectra of 2,3,7,13,17,18-hexamethyl-8,12-diethylcorrole $H_3(\beta\text{-Me}_6\text{Et}_2)\text{Cor}$ **5** in benzene (1), DMF (2), 0.13M Et_2NH in DMF (3), 0.01M $[\text{Bu}_4\text{N}]\text{OH}$ in DMF (4) [26]

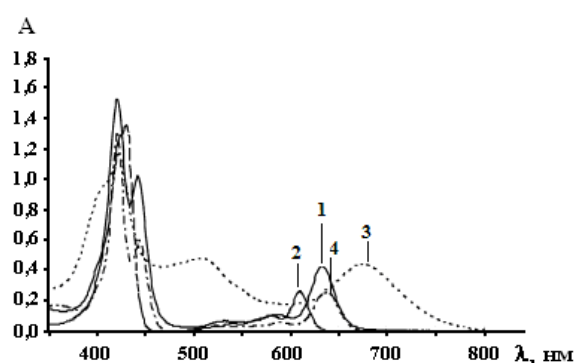


Fig. 9. UV-Vis spectra of *meso*-substituted corroles in dichloromethane-triethylamine media: 1 – 5,10,15-triphenylcorrole **7**, 2 – 5,10,15-tris(pentafluorophenyl)corrole **6**, 3 – 5,10,15-tris(4-nitrophenyl)corrole **8**, 4 – 5,10,15-tris(4-methoxyphenyl)corrole **9** [141]

Meso-substituted π -electron-rich corroles $H_3(\text{ms-Ph})_3\text{Cor}$ **7** and $H_3(\text{ms-4-MeOPh})_3\text{Cor}$ **9** also react with polar dimethylsulfoxide (DMSO) ($\text{DN}=29.8$; $\epsilon=46.7$) and DMF ($\text{DN}=26.6$; $\epsilon=36.7$), but not with low-polar pyridine (Py) ($\text{DN}=33.1$; $\epsilon=12.3$). Electron-deficient macrocycles, for example $H_3(\text{ms-4-NO}_2\text{Ph})_3\text{Cor}$ **8** exist as H-associates even in the environment of such weak electron-donors as acetone $\{(\text{Me})_2\text{CO}$, $\text{DN}=17.0$; $\epsilon=20.7$ } and acetonitrile $\{\text{MeCN}$, $\text{DN} = 14.1$; $\epsilon = 36.0\}$. In the latter case, the process can be time-consuming, i.e. when dissolved, a neutral form is formed first, and when the solution is stored, it becomes an H-associate.



Typical for UV-Vis spectra of H-associates of *meso*-substituted corroles are the Soret band split into two components and a pronounced band at around 640–645 nm in the visible region (Fig. 9). In the case of 5,10,15-tris(pentafluorophenyl)corrole **6**, the Q-band is hypsochromic shifted, and in the case of 5,10,15-tris(4-nitrophenyl)corrole, the band is more wide-broadening in the visible region and located at around 689–696 nm depending on the nature of the solvent; in addition, in this case there is a wide-broadening band at 512–519 nm (Fig. 9). The UV-Vis spectra of anionic forms of *meso*-substituted corroles resemble those of H-associates, differing only in band intensity.

In low-polar environments (C_6H_6 - DMF), the tangents of the slope angle of the indicator dependencies $\lg \text{Ind} = f(C_{\text{solv}})$, corresponding to the number of electron-donor molecules n participating in the interaction, usually exceed one (Fig. 10), which indicates the formation of a weakly connected "salvation shell" of a macrocycle. In systems with low polarity, which contain the main component (C_6H_6 - Et_2NH), or in polar environments in the absence of a strong base (MeCN - DMF), there is a convergence of the interaction stoichiometry to 1:1, but low values of stability constants of ABI (acid-basic interaction) products indicate the formation of H-associates in this case too. In polar environments containing a strong base (MeCN - Et_2NH , DMF - Et_2NH), the formation of spectrally distinguishable monoanionic (H_2Cor^-) forms takes place, and in the case of electrondeficient corrole, $H_3(ms-4-NO_2Ph)_3Cor$, dianionic ($HCor^{2-}$) forms as well.

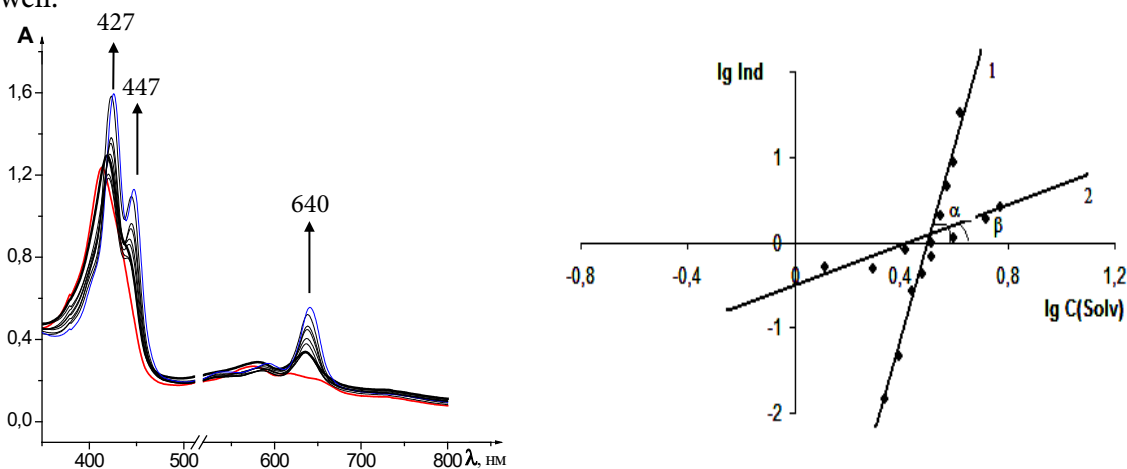


Fig. 10. UV-Vis spectral changes in titration of $H_3(ms-Ph)_3Cor$ **7** in MeCN – (0–6.5M) DMF media, 298 K ($C_{H_3Cor} = 1.92 \cdot 10^{-5}$ mol/l) (left) and indicator dependence graphics for H-associate $H_3(ms-Ph)_3Cor$ **7** and DMF formation: 1) in C_6H_6 ($\text{tg } \alpha = n = 11$); 2) in MeCN ($\text{tg } \beta = n = 1$) – (right)

N-Basicity. Corrole protonation occurs in two stages. When interacting with diluted solutions of strong acids (trifluoroacetic acid, TFA) or acids of medium strength (acetic acid, HOAc), both β - and *meso*-substituted corroles form a single N-protonated form (eq. 3) [35, 39], which has an aromatic character. The second stage of protonation takes place when exposed to sufficiently concentrated strong acids (eq. 4). In the case of β -substituted corroles, it affects one of the *meso*-atoms of carbon (in position 5 or 15) and is accompanied by a disturbance of the macrocycle aromaticity with the disappearance of the Soret band in the UV-Vis spectra [18]. In the case of *meso*-substituted corroles, the Soret band is retained, and the position of the second proton in the macrocycle is not precisely determined, but C-protonation is also the most



probable [26]. At the same time, the basic properties are naturally more pronounced in the corroles containing electron-donor substituents [148].

According to the data [26], both β - and *meso*-substituted corroles are in a single protonated form in the acetic acid medium. In case of β -octaalkylcorrole $H_3(\beta\text{-Me}_6\text{Et}_2)\text{Cor}$ **5**, this form is characterized by two bands in the visible area (580 and 599 nm) and a Soret band at 408 nm; in the case of *meso*-substituted compounds – a split Soret band and a band in the visible region at 670 - 700 nm (Fig. 11, *left*).

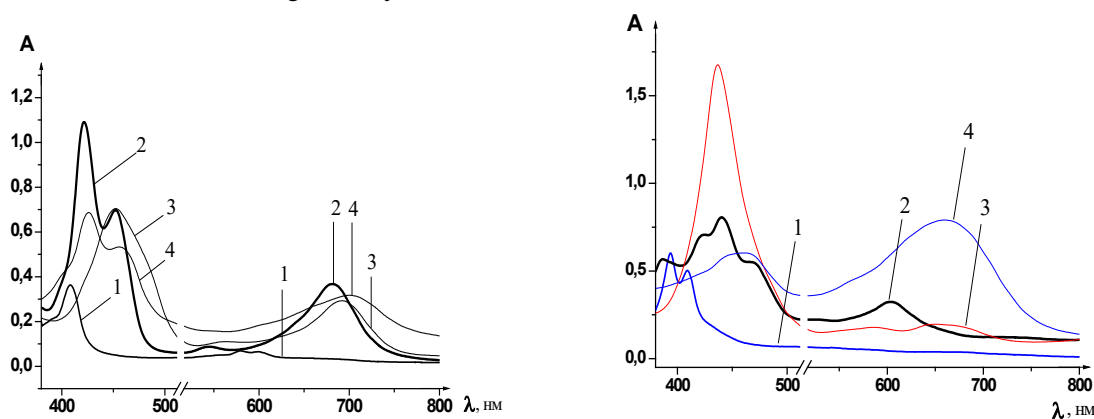
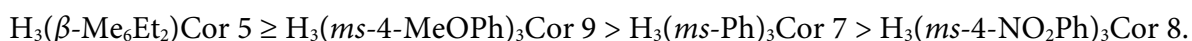


Fig. 11. UV-Vis spectra of monoprotonated (*left*) and diprotonated (*right*) forms of corroles in acetic acid and TFA respectively: 1 – $H_3(\beta\text{-Me}_6\text{Et}_2)\text{Cor}$ **5**; 2 – $H_3(\textit{ms}\text{-Ph})_3\text{Cor}$ **7**; 3 – $H_3(\textit{ms}\text{-4-NO}_2\text{Ph})_3\text{Cor}$ **8**; 4 – $H_3(\textit{ms}\text{-4-MeOPh})_3\text{Cor}$ **9** [26]

In diluted solutions, the interaction of corroles with acetic acid, depending on the type of functional substitution in the macrocycle, runs in the range of concentrations from 0.9 to 17.5 mol/l, and is easier in polar solvents (acetonitrile) and more challenging in non-polar solvents (benzene). However, in the case of protonation competing with the formation of H-associate, the first of these processes runs much worse because it requires the preliminary destruction of H-associate with electron-donor. Therefore, in the case of *meso*-substituted corroles, deviations from this pattern may occur. For the same reason, corrole protonation is relatively difficult in polar but electron-donor environments such as DMF and DMSO.

The authors of [68] show that corrole tautomers are protonated at different speeds, and the nature of the process as a whole, in particular, the type of titration curve, is highly dependent on temperature. Therefore, the stability constants of corrole monocations obtained for 298K in [26, 142] can only be considered as conventional values, which, however, allow us to draw a conclusion about the series of changes in the N-base of compounds, consistent with the ideas about the nature of substituents in the molecules of aromatic heterocyclic macrocycles [11] and the values of proton affinity calculated in [26] by semi-empirical methods. N-basicity of the compounds is reduced as the electron-donor substituents in the $H_3\text{Cor}$ molecule are replaced by electron acceptor groups, and the basic properties of β -octaalkyl-substituted macrocycles at the stage ^{22}N -protoning are higher than those of *meso*-substituted corroles, changing in the series of corroles:





It is also shown that slope angle tangents $\text{tg}\alpha$ of the indicator dependencies obtained in the course of spectrophotometric titration of corroles of different structure, which reflect the number of acid molecules (or number of protons) participating in the reaction, significantly depend on the nature of the environment and are approaching those expected as the titrant strength and polarity of the solvent grow (Fig. 12), for example, in the system MeCN - TFA. The Hammett acidity function H_0 in system C_6H_6 -HOAc also provides a way to obtain tangents of the slope angle of constraint $\lg(\text{Ind}) = f(\lg H_0)$ close to 1, where possible.

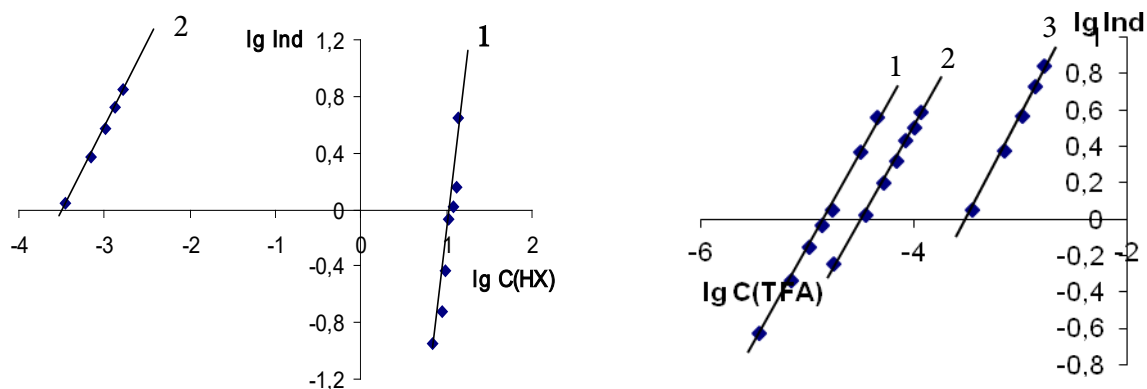


Fig. 12. Indicator dependence graphics for spectrophotometric titration of $H_3(ms-4-NO_2Ph)_3Cor$ **8** in C_6H_6 -HOAc ($\text{tg } \alpha = 4.7$) (1) and MeCN-TFA ($\text{tg } \alpha = 1.1$) (2) media (left, a) and superposition of indicator dependence graphics for $H_3(ms-4-MeOPh)_3Cor$ **9** (1), $H_3(ms-Ph)_3Cor$ **7** (2), and $H_3(ms-4-NO_2Ph)_3Cor$ **8** (3) in MeCN-TFA media ($\text{tg } \alpha \approx 1$ in all cases) (right, b)

In all the cases studied, N-protonation of *meso*-substituted corroles is accompanied by a characteristic change of UV-Vis spectra (Fig. 11) and the bathochromic shift of its Q_x -band, which increases in line with the electron-donor replacement of the molecule from 22 to 45 nm [26, 149, 150].

When corroles interact with pure trifluoroacetic or sulfuric acids, and also their concentrated solutions in organic solvents (the nature of a solvent in this case does not matter a lot), UV-Vis of products corresponds to twice protonated forms (fig. 11, *right*). [26]. The position of the second protonation center is not determined definitively, but it has long been believed that it affects *meso*-positions of a macrocycle [104]. The proof provided is the results of quantum-chemical calculations as well as NMR-spectral studies confirming the non-aromatic structure of the resulting products [26]. UV-Vis spectra type of these forms of corroles is individual for each compound (Fig. 11, *right*). If C-protonation of β -octaalkyl-substituted corrole leads to the disappearance of bands in the visible area, in contrast, in the case of *meso*-substituted corroles, there are intense bands at 600-670 nm in the spectrum. In the environment of concentrated sulfuric acid, the process of formation of two protonated forms of corroles is complicated by the possibility of oxidation of corroles and other adverse reactions. For this reason, UV-Vis spectra of the same corrole in TFA and H_2SO_4 may differ quite significantly [26].

C-protonated or H-associative forms have been repeatedly found in solutions of strong acids in porphyrins themselves (or hyperporphyrins) [151], and in the case of H_2P it is tri-cationic particles of H_4PH^{3+} . In [26] dications H_4Cor^{2+} of *meso*-substituted corroles $H_3(ms-4-MeOPh)_3Cor$ **9**, $H_3(ms-Ph)_3Cor$ **7**, $H_3(ms-4-NO_2Ph)_3Cor$ **8** are recorded spectrally. They are formed



depending on the type of functional group in 4.0-13.5M TFA in the environment C_6H_6 or CH_3CN .

The protonation of corroles should be looked into separately in the cases when the peripheral substituents in their molecules can also attach protons. Thus, when protonating 5,10,15-tris(4-methoxyphenyl)corrole $H_3(ms-4-MeOPh)_3Cor$ **9** in the second stage, the formation of double protonated form is preceded by the formation of the product (exists at $\sim 1.5 \cdot 10^{-3}$ to 4.0M TFA, solvent – C_6H_6 , MeCN, HOAc), which differs in the type of UV-Vis spectrum from both single and double protonated form (Fig. 13), and this transition corresponds to a separate step on the titration curve. It can be assumed that this process is the protonation of peripheral methoxy-groups, which change their nature from electron-donor to acceptor. The latter circumstance explains the relatively low tendency of corrole **9** to form a double protonated form (lower than that of unsubstituted 5,10,15-triphenylcorrole **7**) contrary to theoretical expectations [26].

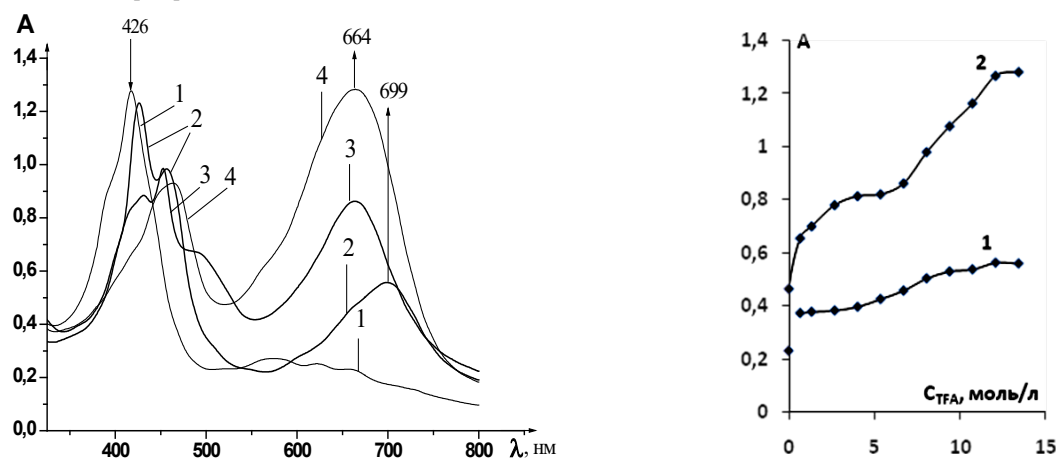


Fig. 13. UV-Vis spectra of 5,10,15-tris(4-methoxyphenyl)corrole $H_3(ms-4-MeOPh)_3Cor$ **9**: H_3Cor (1), H_4Cor+ (2), MeO-protonated H_4Cor+ (3), dication H_4Cor^{2+} (4) (left, a) and titration curves for $H_3(ms-Ph)_3Cor$ **7** (1) and $H_3(ms-4-MeOPh)_3Cor$ **9** (2) (right, b) in the MeCN - TFA media

Dicationic forms of corroles have very significant Stokes shifts of bands in the fluorescence spectra, which is probably due to the non-flat structure of the resulting non-aromatic molecules [11]. So, while in the case of $H_3(ms-4-NO_2Ph)_3Cor$ **8**, $\Delta\nu_{st}$ is 895 cm^{-1} in TFA environment, in $H_3(ms-Ph)_3Cor$ **7** and $H_3(ms-4-MeOPh)_3Cor$ **9** it increases to 1767 and 2420 cm^{-1} , respectively.

Complexation of H_3Cor and reactivity of metallocorroles. One of the most important properties of tetrapyrrolic heterocyclic macrocyclic compounds is their ability to form metal complexes. In the course of reactions of this type, the whole main coordination cavity (CC) of the macrocycle is usually involved in the interaction, which, in symmetrically substituted aromatic molecules, is accompanied by the alignment of "covalent" and "coordination" metal-nitrogen bonds [152].

Porphyryns and related MHC form complexes with the majority of metals of Mendeleev Periodic System, including some non-metals [6]. At the same time, the properties of complexes strongly depend not only on the nature of the complex-forming agent, but also on the properties and peculiarities of the macrocyclic ligand structure. As practice shows, often heterocyclic



macrocyclic compounds show practically significant properties because they have the form of complexes with metals.

The number of chemical elements with which corroles form complexes (MCor) is also quite wide and includes mainly *d*-metals and some non-metals (phosphorus, arsenic) [19]. Corrole complexes with *p*-elements (aluminum, gallium, germanium, tin) [19, 25, 106], as well as rare-earth elements (Fig. 14), are also known.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
*Ln			Ln	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**Ac			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 14. "Periodical Table" of metallocorroles (data of the beginning of 2017) [33]

The absence of the carbon atom in one of the *meso*-positions of the corrole macrocycle leads to a reduction in the size of their coordination cavity compared to porphyrins. The presence of three NH protons determines the "trianionic" nature of H₃Cor ligands, although, like H₂P, corroles are a tetradentate ligand due to the formation of a fourth donor-acceptor bond. As a result, the corroles stabilize unusually high oxidation state of metal in the complexes, ranging from +3 and above. At the same time, the contracted character of the coordination cavity contributes to the placement of cations of smaller radius in the coordination center, i.e. if we talk about one chemical element - cations in a higher oxidation state. This explains the existence of corrole complexes containing Cu(III), Ag(III), Fe(IV), Cr(V), Mn(VI), etc. [49, 58, 153 and others].

Speaking about the tendency of corroles to stabilize high oxidation state of metals in the complexes, a phenomenon should be taken into consideration that foreign authors call "*non-innocence*" [58, 60, 66, 154, etc.]. It means that due to their electronic overabundance, the corroles easily form cation-radical forms. Therefore, it seems unusual at first glance that relatively easy oxidizing compounds – corroles – stabilize metals in high degrees of oxidation, which clearly have an oxidizing ability. The explanation for this phenomenon lies in the fact that corroles in complexes often exist in the cation-radical form, and metal cations only *formally* have an unusually high degree of oxidation, because between the macrocycle and metal cation there is an equilibrium (5), which is in itself the transfer of the electron from the macrocycle to the metal:



The literature pays quite a lot of attention to this issue [49, 58, 154, etc.], but there is no consensus on the neutral ("*innocent*") or cation-radical ("*non-innocent*") nature of the ligands within MCor. As resistance of corroles to oxidation and oxidizing properties of metal cations differ from each other, even in similar complexes the state of the ligand may differ.



Corrole metal complexes are prone to the extraction of electron-donor solvent molecules, which may also be accompanied by a change in the degree of metal oxidation and a marked change in the electron absorption spectrum.

Complexes of *meso*-substituted corroles with metals in high oxidation state {Cr(V), Mn(V), Fe(IV), etc.} are of great interest as new effective catalysts for various processes – redox, group transfer, etc. [17, 22, 155]. Similar complexes with porphyrins are unknown {Cu(III)}, unusual {Co(IV)} or stable only at low temperatures {Fe(IV), Ni(III)} [17, 155].

There are two main methods for the synthesis of corrole complexes – cyclization of biladienes-*a,c* in the presence of metal salt, and direct interaction between the free-base corrole and the metal-containing compound. The nature of the metal ion when synthesized by the first of these methods is crucial: in the presence of ions of some metals, the formation of the macrocycle of a corrole is not observed (as in the case of Zn²⁺) [18], or the corrole is obtained as a free-base (Cr³⁺, etc.) [18, 155]. The first method is applicable for obtaining β -substituted corrole complexes, the second one – for complexes of both β - and *meso*-substituted compounds. Obviously, the second approach to synthesis gives higher yields of the complexes.

One of the nontrivial problems of the coordination chemistry of corroles is the selection of conditions for the dissociation of corrole complexes in proton donor media to the free-base ligand [82]. The process is complicated by side reactions, and often when exposed to strong acids, corrole complexes do not form a protonated ligand form, but completely different products. In addition, even in the case of dissociation of the complex prior to the ligand, the separation of the latter from the reaction mixture, for example, in the case of copper(III) complexes, is often very difficult because of its tendency to re-interact with the salt of the metal formed by dissociation when trying to dilute or extract the reaction mass. Only the first steps have been taken in this direction [25]. Obviously, this problem requires further comprehensive study.

A great number of works [19, 23-25, etc.] are devoted to metallic complexes of corroles, therefore detailed consideration of types of these compounds, their spectral characteristics, and reactivity within one review is rather difficult. Still, it should be noted that there are even more differences in physical and chemical characteristics and chemical behavior of metal complexes of corroles sometimes than similarities, so each compound deserves a separate review. General properties of corrole complexes are the same: even greater wide-broadening of UV-Vis spectra as compared to free-bases (up to complete absence of expressed bands in the visible spectrum area); a high tendency to extracoordinate (mainly electron-donor molecules), which is accompanied by a pronounced change in UV-Vis spectra and the emergence of new bands in it; rarity of dissociation in proton donor environments to the free-base corrole (in the vast majority of cases other products are formed). Let us consider in more detail some perspectives of practical use of these compounds.

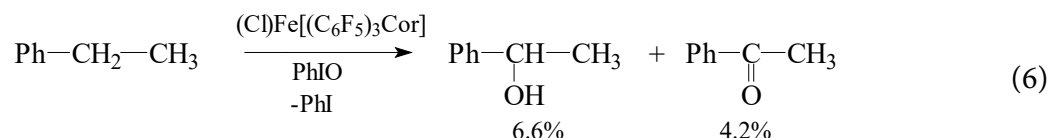
Main areas of practical use of corroles

Most studies in the field of practical application of corroles were carried out using highly stable 5,10,15-tris(pentafluorophenyl)corrole **6** and its derivatives; in particular, complexes with different metals (see [22, 24]). However, other corroles are no less interesting in terms of



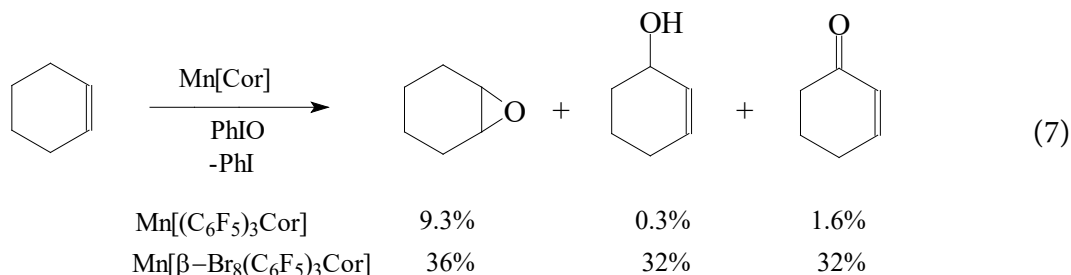
their practical use. The main areas of potential use of corroles and their metal complexes are catalysis, the production of sensors and solar panels, and biomedicine.

Catalysis, photo and electrocatalysis by metallocorroles. Complexes of 5,10,15-tris(pentafluorophenyl)corrole **6** with iron and manganese ($\text{ClFe}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ and $\text{Mn}[(\text{C}_6\text{F}_5)_3\text{Cor}]$) catalyze oxidation of ethylbenzene by iodosobenzene to form a mixture of alcohol and ketone [156, 157] (eq. 6):



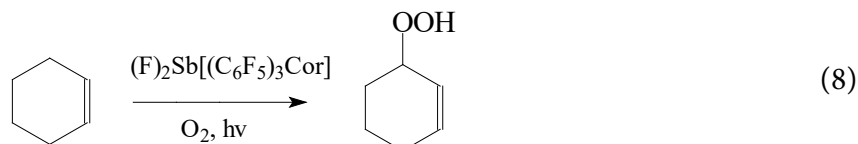
Porphyrin complexes, however, provide higher yields (15.7% and 8.9% respectively).

The complexes of β -octahalogen-*meso*-tris(pentafluorophenyl)corroles with manganese(III) were studied as catalysts for oxidation of cyclohexene with iodosobenzene [44, 158]. These complexes showed good catalytic activity, but the selectivity of the process was not high: as a result, a hard-to-divide mixture of alcohol, ketone, and epoxide was formed (eq. 7):



Due to the impossibility at this stage to increase the selectivity of the process, there have been no systematic studies of catalytic oxygen oxidation of hydrocarbons, but it has been shown that the rate of oxygen atom transfer in the case of metallocorroles is higher than in the case of metalloporphyrins [159].

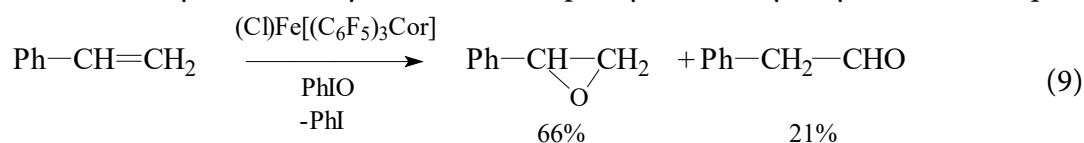
Another approach to efficient and selective hydrocarbon oxidation process is possible: oxidation with singlet oxygen $^1\text{O}_2$, which is formed during the photo-excitation of diamagnetic metal complexes of corroles. In particular, it has been shown that corrole complexes with antimony are effective catalysts for photo-oxidation of organic molecules by ambient oxygen [160]. Under these conditions, hydrocarbons are selectively oxidized to hydroperoxides, and oxidation does not affect the double bonds: styrene does not react, and the oxidation of cyclohexene and cyclooctene takes place only in the allylic position (eq. 8):



The most effective catalyst is the complex $(\text{F})_2\text{Sb}[(\text{C}_6\text{F}_5)_3\text{Cor}]$; complexes $(\text{Py})\text{Sb}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ and $\text{O}=\text{Sb}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ are less effective [160]. The most effective catalyst has the longest life time of triplet state [161], which is one of the determinants of the increase of singlet oxygen yield.

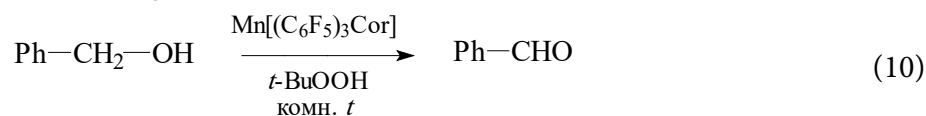


Metal complexes of corroles can be catalysts for epoxidation of alkenes. Thus, styrene at the oxidation of iodosobenzene in the presence of 1 mol. % of the complex $(\text{Cl})\text{Fe}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ formed a mixture of styrene oxide (yield - 66%) and phenylacetaldehyde (yield - 21%) (eq. 9):

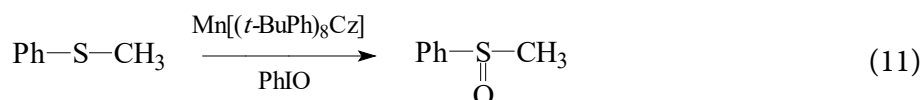


The complexes of 5,10,15-tris(pentafluorophenyl)corrole **6** and its β -octagalogen derivatives with manganese also have catalytic properties in reactions of this type [157, 44, 158, 159, 162, 163].

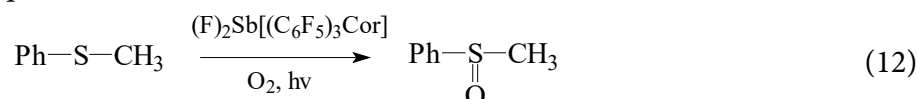
The paper [164] demonstrates the possibility of selective oxidation of alcohols to carbonyl compounds with the help of *tert*-butyl hydrogen peroxide in the presence of complexes of electron-deficient corroles with manganese (III) (eq. 10), for example:



In [163] the oxidation of thioanisole by iodosobenzene and *p*-cyanodimethylaniline oxide in the presence of octa-(4-*tert*-butylphenyl)corrolazine complex with manganese(III) was studied (eq. 11):



Good catalysts for photo-oxidation of thioanisole by singlet oxygen in alcohol solutions are the already mentioned complexes of 5,10,15-tris(pentafluorophenyl)corrole **6** with antimony [160]. The only oxidation product in this case is sulphoxide; no further oxidation into sulfone is observed (eq. 12):



Due to the stabilization of corroles with high levels of oxidation of metals in the complexes [24], corrole complexes with metals in low oxidation states should be very reactive. Therefore, it is reasonable to expect that they will demonstrate the unique properties associated with the activation of small molecules. However, so far this area has been relatively unexplored.

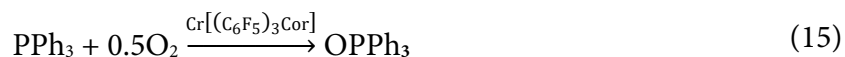
In [165] the complexes of corroles with chromium in four degrees of oxidation have been obtained, and it is shown that the complex of chromium(III) $\text{Cr}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ is capable of oxidizing by oxygen to the chromium oxocomplex(V) $\text{O}=\text{Cr}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ (eq. 13):



Inspired by these results, the authors [166] made a successful attempt to use chromium complexes of corroles as catalysts for oxidation of organic substrates with ambient oxygen. In particular, triphenylphosphine was oxidized to the triphenylphosphine oxide by the oxocomplex $\text{O}=\text{Cr}[(\text{C}_6\text{F}_5)_3\text{Cor}]$, which was restored to the complex of chromium(III) $\text{Cr}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ (eq. 14):

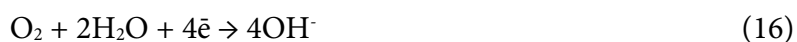


The total of the equations of the last two reactions (eq. 13-14) gives the equation of oxidation of triphenylphosphine by ambient oxygen in the presence of complex $[(\text{C}_6\text{F}_5)_3\text{Cor}]\text{Cr}$ as a catalyst (eq. 15):



The corresponding β -brominated chromium(V) oxocomplex is capable of oxidizing reactive olefins of norbornen type to epoxides, but the reduced form of the complex is difficult to oxidize with ambient oxygen.

Electrochemical studies of corrole complexes with cobalt and iron were carried out in [167], and it was shown that the reduction of molecular oxygen always goes to water using a four-electron mechanism, without the accumulation of less reduced peroxide intermediates (eq. 16):

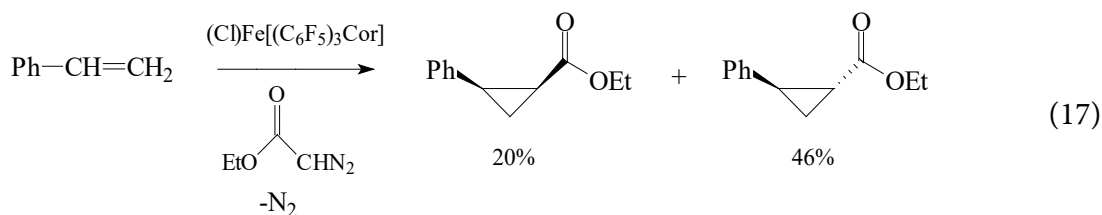


Obviously, the data [167] indicate a high efficiency of the use of metallocorroles in electrocatalysis and correspond to the also studied ability of these compounds to catalyze the decomposition of hydrogen peroxide [168, 169].

The works [26, 32, 170-173] studied the electrochemical properties of *meso*-substituted corroles and their complexes with *d*-metals (Cu(III), Zn(II), Co(III), Mn(III), Fe(IV)) in an inert atmosphere, as well as the catalytic activity of these compounds in the electroreduction of molecular oxygen in 0.1M aqueous solution of potassium hydroxide saturated with O_2 . It should be noted that the interest in the catalytic properties of compounds in the reaction of electric reduction of oxygen is due to the possibility of creating new low-temperature power sources on their basis. The system in which the measurements are taken was also chosen in accordance with the practical tasks, namely the aqueous-alkaline solution, which is similar to the alkaline batteries already in use.

Comparison of the electrocatalytic activity of complexes of the same metal with corroles containing substituents of different electronic nature allows us to conclude that in most cases the presence of electron-donor substituents in the molecule contributes to the improvement of electrocatalytic properties. If we talk about the electrocatalytic activity of complexes depending on metal, the most active are corrole complexes with manganese and iron. Compared to similar complexes of porphyrins, the electrocatalytic activity of corrole complexes is slightly higher.

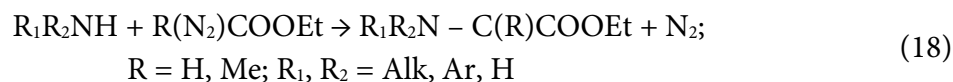
It was shown that the complexes of iron with 5,10,15-triphenylcorrole **7** and 5,10,15-tris(pentafluorophenyl)corrole **6**, as well as complexes of rhodium with *N*-substituted corroles are effective catalysts for the reaction of "cyclopropanation" of styrene with ethyldiazoacetate. This is not the first example of a reaction in which corroles are more effective as catalysts than the corresponding porphyrins, where the yield of products is somewhat lower and is 7 and 40%, respectively [24, 156] (eq. 17):



One of the reasons for the higher catalytic activity of corroles in this reaction as compared to porphyrins is the absence of one of the aryl groups, which spatially favors the formation of intermediates. In addition, the degree of iron oxidation in complexes is important: in the case of porphyrins, initial reduction of iron(III) complexes is necessary, while corrole complexes with iron(III) themselves are direct catalysts of the process. In case of corrole complexes with iron(IV), their initial reduction to iron(III) complexes is necessary. It should be noted that when iron complexes with both porphyrins and corroles are used as catalysts, there is a side process of dimerization of ethyldiazoacetate with the formation, mainly, of diethylmaleate. In the case of rhodium complexes, the course of the side process is weaker [174]. However, rhodium complexes with sterically hindered corroles are less effective catalysts than complexes containing small substituents. Rhodium complexes give high products yields, but the ratios of *trans*- and *cis*-products in this case are smaller than in the case of iron complexes and are comparable to the values observed in the case of porphyrins.

The authors [22] described the possibility of introducing a fragment of carbene (from ethyldiazoacetate) by the allylic position of cyclohexene, dihydronaphthalene, and indene. When the complex $(PPh_3)Rh[(C_6F_5)_3Cor]$ was used as a catalyst, the yields of the desired products were not too high, and the main products of the process were the corresponding derivatives of cyclopropane formed by the double bond reaction [22]. At the same time, rhodium complex proved to be a more suitable catalyst for the process in comparison with iron complexes, in the case of which only dimerization products of ethyldiazoacetate are formed.

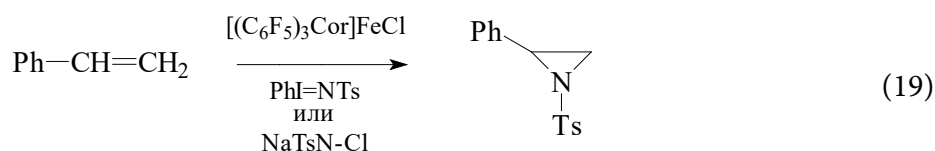
At the same time, the complexes of iron $(Cl)Fe[(C_6F_5)_3Cor]$ and $(OEt)_2Fe[(C_6F_5)_3Cor]$ effectively catalyze the connection of diazoacetate (with nitrogen detachment) via NH-bonds of amines [175]. The corresponding N-substituted ethyl esters of glycine (or alanine) are formed this way (eq. 18):



These complexes catalyze this reaction better than other metal-corroles and other previously studied catalysts. The reaction when exposed to complexes of 5,10,15-tris(pentafluorophenyl)-corrole with iron runs selectively through NH-bonds even in the presence of olefins.

It is necessary to notice that the similar phenomenon is observed also for complexes of porphyrins with iron, but the latter give somewhat less selectivity of process, and for primary amines, traces of the disposed product are formed. However, when using ammonia [176] in the presence of the complex $(OEt)_2Fe[(C_6F_5)_3Cor]$, only traces of aminoacid esters were formed, while the iron(III) complex with tetraphenylporphine gives a higher yield.

Reactions of olefins and, in particular, styrene with compounds $PhI=NTs$ and $NaTsN-Cl$ with the formation of aziridines were also studied in the literature [177-179] (eq. 19):



It has been shown that iron complexes with corroles are more effective catalysts for the reaction of styrene with PhI=NTs compared to the corresponding porphyrin complexes, having, in particular, higher selectivity. In both cases, the by-products are styrene oxidation products - styrene oxide and phenylacetaldehyde.

In the case of the reaction with chloramine T (NaTsN-Cl), only the complex $[(\text{C}_6\text{F}_5)_3\text{Cor}] \text{FeCl}$ shows catalytic activity, and no oxidation by-products of olefin are formed. The reaction of aziridine formation from olefin when exposed to chloramine T catalyzed by $(\text{Cl})\text{Fe}[(\text{C}_6\text{F}_5)_3\text{Cor}]$ is the first example of such a process where the transition metal in the catalyst is not a copper atom [178, 179].

In [180], it is demonstrated that complexes of *meso*-substituted corroles with iron catalyze copolymerization of epoxides with carbon dioxide while forming crystalline polymers.

Chemosensorics. There have been attempts to study metal complexes of corroles as sensors. For example, it was found [181] that corrole complexes with cobalt(III) can bind carbon monoxide CO. In addition, cobalt(III) complexes were found to be inert with respect to molecular oxygen. It stimulated researchers to explore complexes as potential carbon monoxide sensors. It has been demonstrated that the efficiency of CO binding depends on the electron density at the metal atom: the higher it is, the worse the CO binds. In particular, the complex of cobalt(III) with electron excess β -octaethylcorrole **4** does not react at all with CO, while the complex with 5,10,15-tris(pentafluorophenyl)corrole **6** shows the highest affinity for carbon monoxide [181]. Comparison of metal complexes of corroles with porphyrinic analogues in respect of CO binding efficiency paves a way to draw a conclusion about a very high selectivity of corrole complexes in relation to carbon monoxide in the presence of oxygen, which is not observed for other macrocycles. The work [182] reported successful attempts to immobilize corrole complexes with cobalt on silica gel in order to create chemical sensors on CO.

Corrole complexes with manganese were studied as potential sensors for organophosphorus compounds. It was shown that these complexes form accession products with organic phosphonates by the type of composition extracoordination at rate 1:1, which is easily detected by EAS changes [183].

Corroles are very promising materials for creating optical pH-sensors (optodes), because at different pH values they can exist in the form of different protonated forms with different fluorescence intensity [184]. The work [185] attempted to create a fluorescent optical pH-sensor based on 10-(4-aminophenyl)-5,15-dimesitylcorrole. The optode membrane on which the corrole was immobilized demonstrated a linear response in the pH range of 2.2 - 10.3, while the inorganic ions in the solution had little influence on the pH determination accuracy. The optode kept its properties while wet for a long time, demonstrating good reproducibility and high photostability. The range of pH values measured with this optode on the basis of 10-(4-aminophenyl)-5,15-dimezitylcorrole was significantly wider than with 5,10,15-tris(pentafluorophenyl)corrole **6** (5.0 to 9.2) or tetraphenylporphine (3.3 to 5.0).



The same scientific group studied the possibility of using a polyvinyl chloride membrane containing 5,10,15-tris(pentafluorophenyl)-corrole **6** as a sensitive element of the silver electrode [186]. The corrole-based electrode has shown noticeably better characteristics compared to its analogue based on tetraphenylporphine: In particular, linear response in the range of Ag^+ $5.1 \cdot 10^{-6}$ - $1.0 \cdot 10^{-1}$ mol/l, fast response time (less than 30 s), operating range pH 4.0 - 8.0. The electrode demonstrated high selectivity and proved to be very easy to manufacture and use, in particular, to determine silver in real ore samples. A similar electrode can be used to determine mercury(II) [187]. It has a linear response in the range of Hg^{2+} $1.2 \cdot 10^{-7}$ - $1.0 \cdot 10^{-4}$ mol/l, operating range pH 5.0 - 8.0, and a response time of about 5 min.

The possibility of using corroles in liquid diaphragm electrodes can be used at potentiometric determination of phenols in an aqueous-organic medium [188]. The key factor in the recognition of phenols here is the high NH-acidity of corroles. As it turned out, the sensitivity of the electrode to phenols decreases in the row *p*-nitrophenol - *m*-nitrophenol - *o*-nitrophenol and 2,4-dinitrophenol - 2,5-dinitrophenol - 2,6-dinitrophenol. Since phenols were recognized in non-ionized form, this indicates the formation of molecular complexes between them and the corroles. In [189], the influence of additives of salts, as well as acid-basic properties of phenols and corroles on the force of molecular complexation was studied, and as a consequence, the efficiency of phenol determination under different conditions.

The literature contains data on the use of corroles to create ion-selective electrodes. In particular, the authors [190] report on the first potentiometric sensor sensitive to both salicylic acid and salicylate ion. The minimum detectable salicylate concentration of about 10^{-5} mol/l allows the use of corrole-based ion-selective electrodes in various systems, and a fairly wide range of concentrations and low influence of other ions makes it possible to determine salicylates directly in biological fluids.

2,17-disulfo-5,10,15-tris(pentafluorophenyl)-corrole as well as its complexes with gallium(III) and tin(IV) have been tested as active components for creating solar batteries [191]. Although the tin complex has shown less activity than the gallium complex and the free ligand, it has been shown that corroles are generally more effective as photoconverters than other tetrapyrrole heterocyclic macrocycle compounds.

Biomedicine. It should also be noted that the application of corroles and its metal complexes in medicine is promising. They can be used as inhibitors of chronic oxidative stress leading to neurodegenerative pathologies, such as Alzheimer's or Parkinson's disease, which are as yet poorly treatable [24, 192]. At the same time, the use of corroles in this field of medicine is still only a rather distant prospect, although appropriate patents for the use of these substances have already been obtained (see, in particular, [193]). The use of heterocyclic macrocycles and, in particular, corroles as a means of fluorescent diagnostics (FD), chemo- (CT), and photodynamic therapy (PDT) of various neoplastic processes and bacterial infections [194-205] attracts the researchers' greatest attention. It was found that metal complexes (in particular, with gallium) of the above mentioned corroles with anionic groups, in particular, amphiphilic 2,17-disulfo-5,10,15-tris(pentafluorophenyl)corrole, have a pronounced cytotoxic and/or cytostatic effect on a number of lines of atypical cells (melanoma, breast cancer, and ovarian cancer) [197]. In [203, 204], the possibility of using cationic and anionic corroles for suppression of life



activity of different microorganisms by PDT was studied, in particular, for destruction of mold fungi and their spores, as well as for effective photoinhibition of green algae culture growth and biofilms based on them. PDT in this case is a good alternative to the use of various antibiotics and antiseptics. It is important that microorganisms do not produce the mechanisms of resistance to the action of active oxygen forms generated by PS, and biofilms, which significantly narrow the possibilities of antibiotic therapy, are effectively eliminated [205].

Thus,

1. Corroles are tetrapyrrole heterocyclic macrocycle compounds, intermediate in structure between porphyrins and corrins. Corroles have the same structure of a carbon skeleton molecule as corrins and the same aromaticity as porphyrins. The structure of the coordination center of corrole molecules is described by the schematic formula N_4H_3 , which helps to stabilize these compounds of metal ions of high oxidation degrees.

2. As with the related series of porphyrins, there are variously modified compounds in the corrole series. Depending on the type of substitution in the macrocycle (β - or *meso*-substituted compounds) and the nature of substituents in the macrocycle (electron-deficient or electron-substituted compounds), the corroles show a rather large variation in physical and chemical characteristics and reactivity.

3. There are various synthetic approaches to corrole production, and the method of synthesis of a particular compound must be selected based on its structure. One method may be well suited to the synthesis of one structural type of corrole and be of little use for another. There are methods to modify functional groups already present in the corrole molecule, which further expands the possibility of obtaining corroles with predetermined properties.

4. Compared to porphyrins, corroles have a number of features (narrowed coordination cavity in the presence of three NH-protons, π -electron excess of the macrocycle) which lead to a noticeable change in the properties of H_3Cor in comparison with H_2P . Corroles in the form of free ligands are NH-active compounds prone to unfinished acid-base interactions with both electron-donor and proton-donor solvents, and the NH-activity depends on the type of substitution in the macrocycle and the electronic nature of the substituents.

5. Corroles are stabilized by high levels of oxidation of metals in complexes, but reversible electronic transitions between the metal atom and π -system of the macrocycle are also possible, resulting in the formation of cation-radical forms of ligand. Metal complexes of corroles are prone to the extraction of electron-donor molecules, and under the influence of acids only in rare cases dissociate to a free ligand, forming for the most part completely different products.

6. Corroles and their metal complexes are promising as new catalysts in the processes of decomposition of peroxides, oxidation (alkanes and alkenes, sulfides, phosphines, etc.) and reduction (oxygen, CO_2) of various substrates, group transport reactions, as sensors (amines, CO, etc.) and components of ion-selective electrodes, converters of light energy into electrical energy, as well as means for photodynamic therapy in medicine.

The work was supported by RFBR grant Bel_a No. 20-53-00038.



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Received 11.09.2020

Accepted 15.10.2020