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Tetrabenzotriazaporphyrins: synthesis, properties and application

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Synthetic approaches to tetrabenzotriazaporphyrins and their complexes with metals and semimetals (P, Si) are considered. Methods for complexation of free-base tetrabenzotriazaporphyrin ligands and the preparation of water-soluble derivatives *via* the introduction of a sulfo group are analyzed. Particular attention is given to investigations of this class of compounds by electronic absorption spectroscopy and possibilities of their practical application.
The bibliography includes 80 references.

Contents

I. Introduction 657
II. Methods for the synthesis of tetrabenzotriazaporphyrin derivatives 658
III. Electronic absorption spectra of tetrabenzotriazaporphyrins and their complexes 670
IV. Application of tetrabenzotriazaporphyrins and their complexes 674
V. Conclusion 674

I. Introduction

Phthalocyanine (PcH_2, **1**) and its analogues belong to a broad class of macrocyclic tetrapyrrole compounds. The synthesis of phthalocyanines was first mentioned early in the 20th century. In 1907, Braun and Tcherniac [1] isolated a blue substance upon heating of *o*-cyanobenzamide in ethanol. However, it is commonly recognized that Linstead was a pioneer in the chemistry of phthalocyanines. He was the first to study in detail the main properties of this class of compounds.[2] The latter have attracted interest not only due to their unique physicochemical characteristics but also due to their structural similarity with many important natural compounds (chlorophyll, haemoglobin, cytochrome *c*) involved in vital processes in living organisms, such as cellular respiration, photosynthesis, electron transport, *etc*. Unsubstituted phthalocyanines are characterized by low solubility in most organic solvents, which substantially limits their studies.

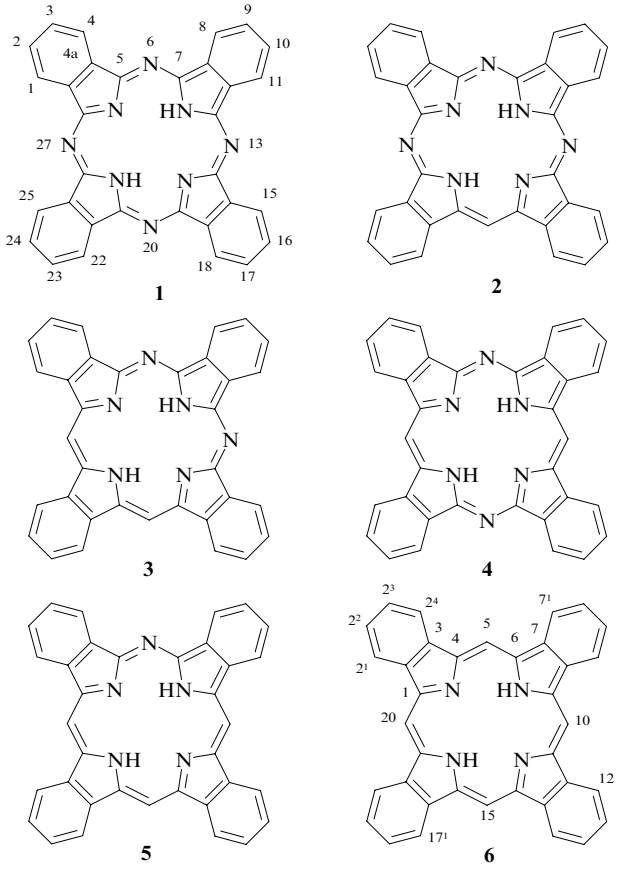
One of the main methods for the functionalization of phthalocyanine is based on the introduction of substituents into benzene rings, resulting in a substantial increase in the solubility of new compounds. Another method suitable for modifications is to replace bridging nitrogen atoms by one or several methine moieties. This approach was employed to prepare structures **2**–**5**. Historically, there are two nomenclatures used to name such macrocyclic compounds, which are considered as either phthalocyanine or tetrabenzoporphyrin derivatives. However, the atomic numbering scheme of the phthalocyanine type is more commonly used for tetrabenzotriazaporphyrin [$(TBTAP)H_2$, **2**], *cis*- and *trans*-tetrabenzodiazaporphyrins [$(TBDAP)H_2$, **3** and **4**, respectively] and tetrabenzomonoazaporphyrin [$(TBMAP)H_2$, **5**].

In addition to phthalocyanine, tetrabenzoporphyrin derivatives [$(TBP)H_2$, **6**] are the most well-known structures of the above-mentioned type. The chemistry of the latter compounds has been actively developed since 1981.[3] Although first results of studies of macrocyclic compounds **2**–**5** have been reported soon after the publication by Linstead,[2] data on tetrabenzotriazaporphyrin derivatives are scarce in the literature, and reviews focused on such macrocycles are absent. This is due both to a limited number of syntetic methods and difficulties of their isolation from a mixture of products. Indeed, the synthesis of these compounds can afford up to five structurally similar macrocycles.

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Current research interests: synthesis and investigation of properties of phthalocyanines, benzoporphyrin analogues and their metal complexes.

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Structures 1–6

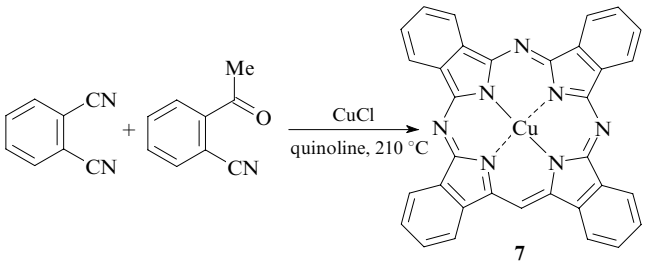


The goal of the present review is to survey available methods for the synthesis of tetrabenzotriazaporphyrins, as well as the characteristic features of their complexation with metals and metalloids. The spectral characteristics of these compounds are considered in detail and the fields of practical application of these compounds are discussed.

II. Methods for the synthesis of tetrabenzotriazaporphyrin derivatives

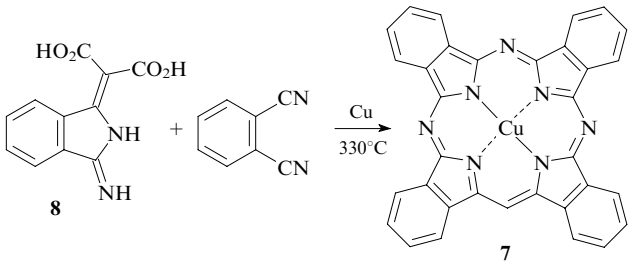
The first synthesis of tetrabenzotriazaporphyrin was published in 1937. Helberger and von Rebay [4] performed the reaction of phthalonitrile (1,2-dicyanobenzene) with *o*-cyanoacetophenone in an equimolar ratio in the presence of copper(I) chloride (Scheme 1).

Scheme 1



After the addition of pyridine to the reaction mixture, product **7** precipitated as violet crystals. A decrease in the amount of phthalonitrile with respect to *o*-cyanoacetophenone (the 1.0 : 1.8 ratio) resulted in the isolation of the Cu complex of tetrabenzodiazaporphyrin. It was found that, in the absence of phthalonitrile, the reaction produces the Cu complex of tetrabenzomonoazaporphyrin. More recently, Linstead and *et al.*,[5] who studied this reaction, reported that a mixture of products obtained with the use of phthalonitrile and *o*-cyanoacetophenone in a ratio of 1.0 : 1.77, contains, in addition to (TBDAP)Cu, copper tetrabenzotriazaporphyrin (**7**). The authors suggested using the condensation product of 1,3-diiminoisoindoline and malonic acid (compound **8**) instead of *o*-cyanoacetophenone as the starting compound (Scheme 2).

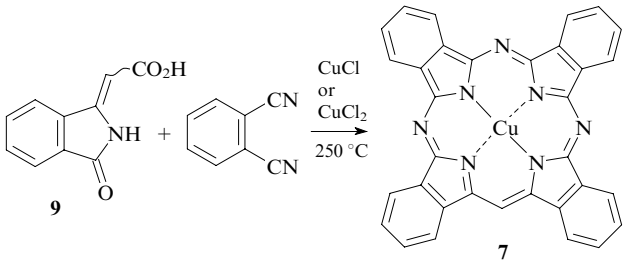
Scheme 2



The fusion of **8** with copper in the absence of phthalonitrile affords a mixture of Cu complexes of TBMAP and TBDAP, whereas the use of zinc or its acetate results in the formation of a mixture of Zn complexes of TBP and TBMAP.[5]

In 1938, another method for the synthesis of (TBTAP)Cu was covered with a patent.[6] Phthalimidineacetic acid **9** or methylenephthalimidine, which can be easily prepared by heating acid **9** in water at 80 °C, served as a source of the methine bridge.[6, 7] The reaction was performed by fusing reagents at 250 °C or by heating under reflux in 1-chloronaphthalene (Scheme 3).

Scheme 3

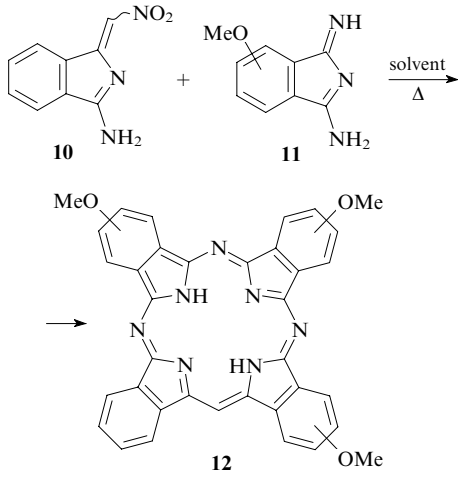


Dent [7] reported preparation of complex **7** in 30% yield. In the reaction with the use of methyl phthalimidineacetate or the corresponding Cu salt instead of phthalimidineacetic acid by itself, the formation of the (TBTAP)Cu was not observed. The reaction with the N-methylated analogue of phthalimidineacetic acid, *viz.*, *N*-methylphthalimidineacetic acid, also does not take place. Although the formation of tetrabenzomonoazaporphyrin derivatives in the absence of phthalonitrile in the reaction mixture was described in two studies,[4, 5] such complexes were not isolated by Dent.[7] It was shown [6, 7] that the similar reaction readily proceeds with the use of 4-chlorophthalonitrile as well. In addition to copper complexes, the synthesis of magnesium, tin and lead tetrabenzotriazaporphyrins was patented.[6]

More recently, the mixed condensation involving 1-amino-3-nitromethylideneisoindole (**10**), which was prepared by the reaction of 1,3-diiminoisoindoline and nitro-

methane in methanol on heating, was suggested to apply for the synthesis of tetrabenzotriazaporphyrin derivatives.[8,9] The condensation was performed by the addition of a mixture of reactants **10** and **11** to preheated high-boiling solvents (xylene, nitrobenzene, *o*-dichlorobenzene, 1-methyl- or 1-chloronaphthalene). The reaction mixture was kept at reflux for 3–24 h (Scheme 4).

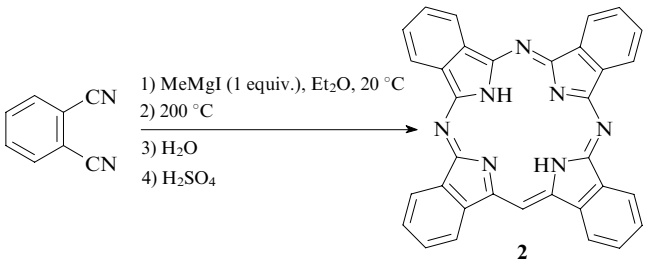
Scheme 4



In addition to compound **11** containing a methoxy group in the benzene ring, this reaction was carried out with unsubstituted isoindoline and the benzannulated derivative.[8] It should be noted that macrocycle **12** and its analogues are almost insoluble in organic solvents and, consequently, they cannot be purified by chromatography.

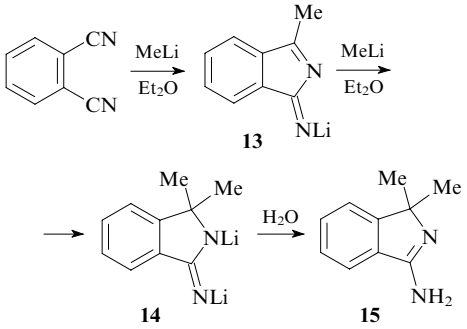
In 1939, the use of an organomagnesium compound as a source of a hydrocarbon bridge in TBTAP was described.[10] This method is based on the addition of methylmagnesium iodide to a solution of phthalonitrile in diethyl ether. After the storage of the reaction mixture at room temperature for several hours, diethyl ether was distilled off and the solid residue was allowed to stand at 200 °C with the gradual addition of water followed by the treatment with H_2SO_4 (Scheme 5).

Scheme 5



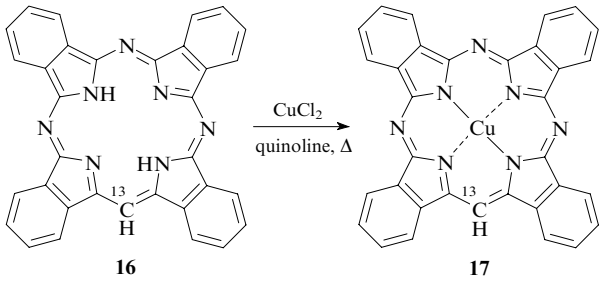
An attempt was made to perform this reaction with methyllithium instead of methylmagnesium iodide.[10] However, this reaction afforded a small amount of a mixture of products containing mainly diaza and monoaza macrocycles. This was explained as follows. Phthalonitrile initially binds one methyllithium molecule to form lithium derivative **13**, and the latter rapidly reacts with the second MeLi molecule. The hydrolysis of dilithium derivative **14** gives 1-amino-3,3-dimethylisoindole (**15**), which cannot be involved in the formation of the macrocyclic system of tetrabenzotriazaporphyrin (Scheme 6).

Scheme 6



The reaction with the labelled reagent $^{13}CH_3MgI$ produced macrocycle **16** enriched in the ^{13}C isotope.[11] The heating of ligand **16** with an excess of $CuCl_2$ in freshly distilled quinoline gave copper complex **17**, and the latter was recrystallized from 1-chloronaphthalene (Scheme 7).

Scheme 7



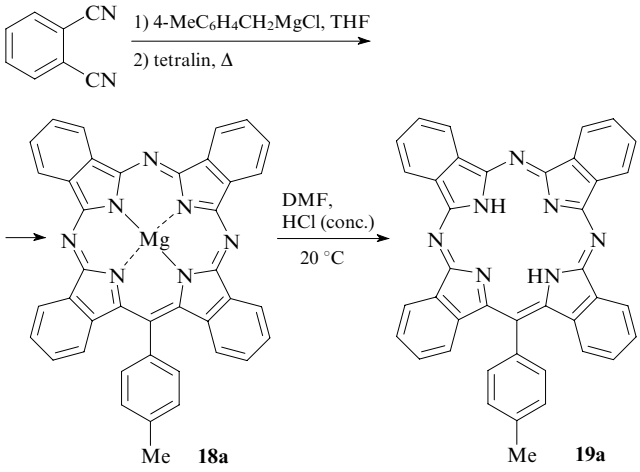
As mentioned above, metal complexes of TBTAP unsubstituted at the *meso*-carbon atom are poorly soluble in organic solvents. These compounds are purified mainly by recrystallization from 1-chloronaphthalene or quinoline. Magnesium and cadmium complexes have the highest solubility among known metal complexes with these ligands.

Kachura *et al.*[12] analyzed methods for the synthesis of aza analogues of tetrabenzoporphyrin published by that time and purified these compounds by chromatography. It was found that Mg and Cd complexes of tetrabenzoazaporphyrins are fairly readily soluble in mixtures containing THF. This allowed the researchers to separate mixtures of reaction products by aluminium oxide column chromatography using a 1 : 3 mixture of THF and trichloroethylene as the most efficient eluent. This method was employed to isolate Mg and Cd complexes of tetrabenzomono- and tetrabenzotriazaporphyrins in the pure form. Metal complexes of diaza derivatives were prepared only as inseparable mixtures of *cis*- and *trans*-isomers. The authors concluded that the macrocycles described early were contaminated with other complexes (for example, with tetrabenzodiazaporphyrins or phthalocyanines) and noted that they were the first to characterize the complex (TBTAP)Mg in the pure state.

The reaction of phthalonitrile with benzylmagnesium chloride instead of methylmagnesium iodide produces only

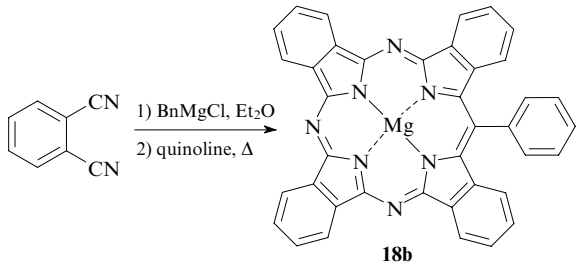
unsubstituted phthalocyanine.[10] In the patent,[13] it was mentioned that the use of the procedure developed by Barrett *et al.*[10] results in the isolation of magnesium phthalocyanine as the only product. A modified procedure producing the 27-(*p*-tolyl) derivative as magnesium complex **18a** was covered with a patent.[13,14] The demetallation of **18a** with concentrated HCl in dimethylformamide affords free ligand **19a** (Scheme 8).

Scheme 8



In 1990, Leznoff and McKeown[15] additionally studied the reaction of phthalonitrile with benzylmagnesium chloride and found that the heating of the product in quinoline at 200 °C for 22 h resulted in the formation of magnesium 27-phenyltetrabenzotriazaporphyrin complex (**18b**) in 15% yield (Scheme 9).

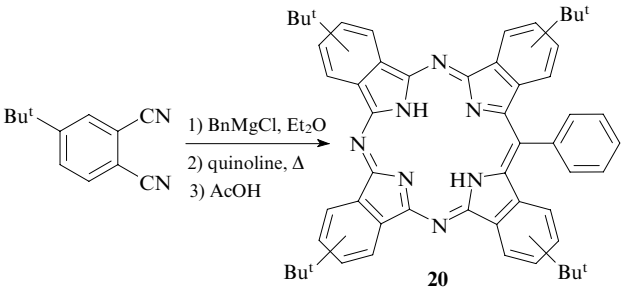
Scheme 9



The authors also mentioned that the free macrocyclic ligand cannot be separated from unsubstituted phthalocyanine obtained as a by-product because of very low solubility of this ligand in organic solvents. On the contrary, Mg complex **18b** is readily soluble in coordinating solvents; hence, it can be purified by chromatography. In addition, the formation of an inseparable mixture of *cis*- and *trans*-isomers of tetrabenzodiazaporphyrins as by-products was observed.

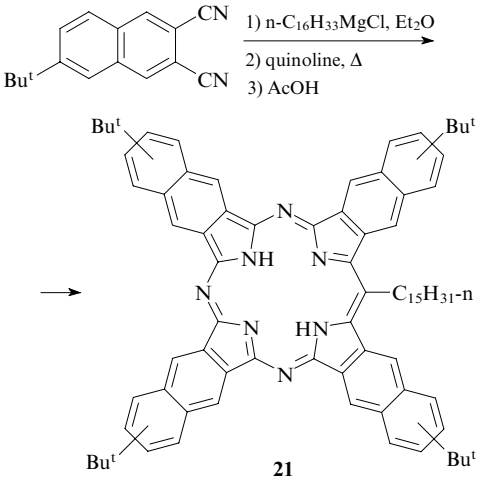
The reaction with the 4-*tert*-butyl derivative of phthalonitrile instead of unsubstituted phthalonitrile affords products having higher solubility, which made it possible to separate these compounds by chromatography and isolate tetra(*tert*-butyl)-substituted tetrabenzotriazaporphyrin **20** as the free ligand.[15] The initially formed Mg complexes were demetallated with acetic acid on heating for 1 h without isolation from the reaction mixture (Scheme 10).

Scheme 10



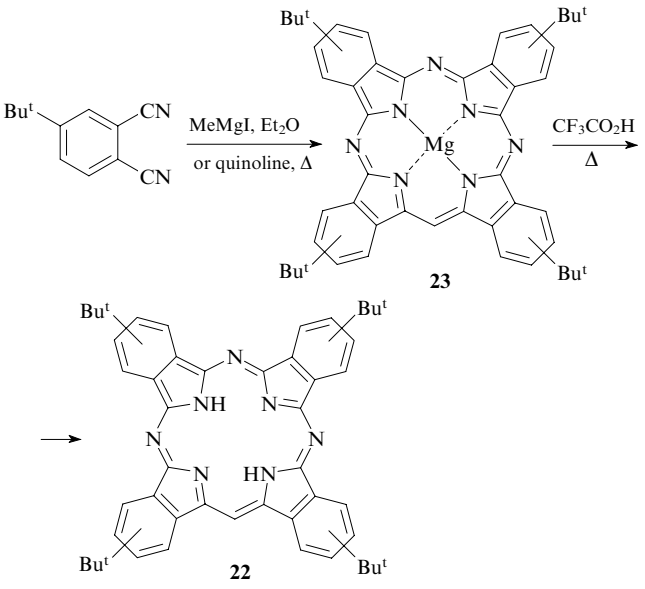
This scheme was also used to synthesize triazaporphyrin based on 6-*tert*-butyl-2,3-dicyanonaphthalene.[15] The yield of complex **21** was as low as 3% because it was difficult to separate this compound from the second reaction product, *tert*-butyl-substituted naphthalocyanine. This is the only example of soluble naphtho-annulated triazaporphyrin (Scheme 11).

Scheme 11

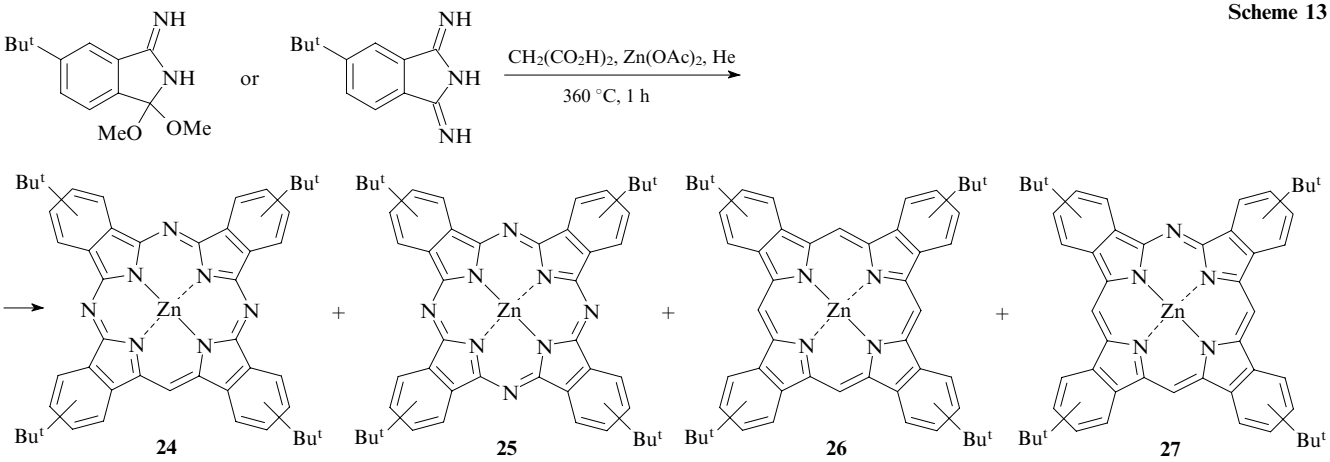


Tetrabenzotriazaporphyrin ligand **22** unsubstituted in position 27 was synthesized from 4-*tert*-butylphthalonitrile

Scheme 12



Scheme 13



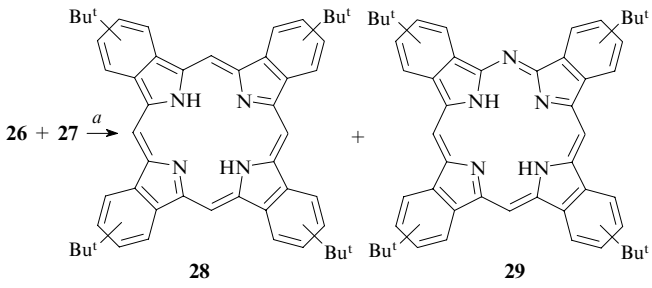
according to the following two procedures: with the use of methylmagnesium iodide[16] or by heating with quinoline (Scheme 12).[15]

Magnesium complexes of tetrabenzotriazaporphyrin (**23**) and phthalocyanine were isolated as the reaction products.[17] They were separated by double chromatography on aluminium oxide using chloroform as the eluent. Complex **23** is easily demetallated on heating in trifluoroacetic acid. The corresponding macrocyclic ligand **22** is also readily soluble in chloroform and was purified by aluminium oxide chromatography. This reaction produced complex **23** in a total yield of 12%.[17]

The chromatographic separation of tetra(*tert*-butyl)tetrabenzotriazaporphyrin **22** and tetra(*tert*-butyl)-substituted phthalocyanine was described by Karasev *et al.*[18] It was suggested to use acidic aluminium oxide as the sorbent for column chromatography, resulting in a decrease in the content of phthalocyanine in the product to 1%.

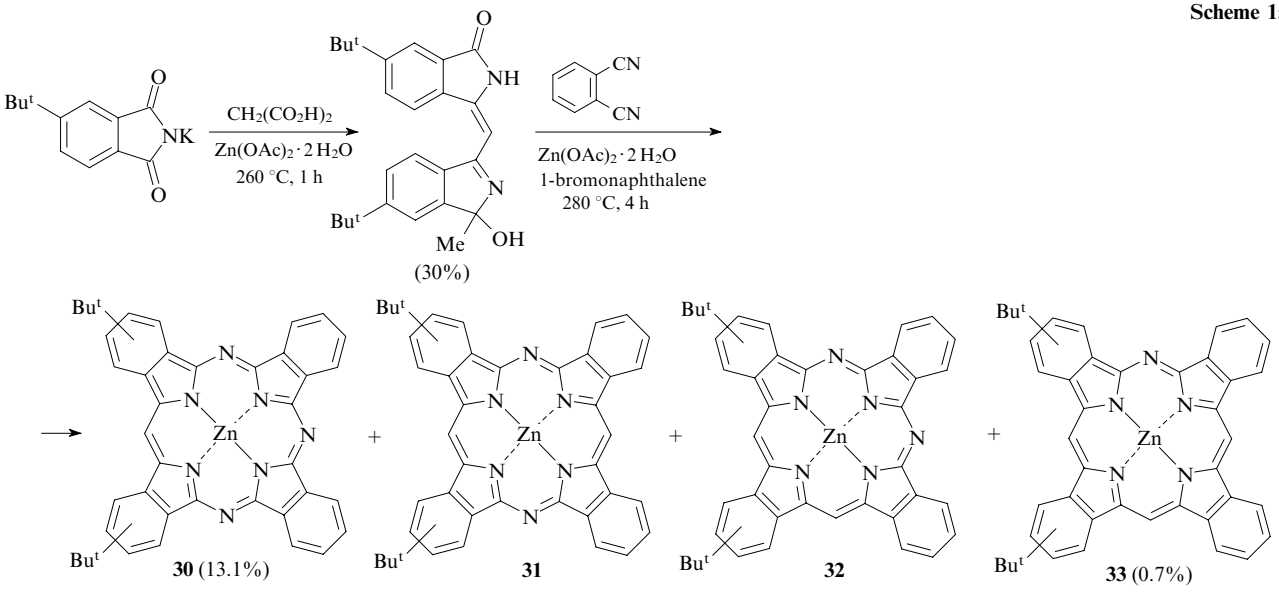
Kopranenkov *et al.*[19] described the synthesis of the Zn complex of tetra(*tert*-butyl)tetrabenzotriazaporphyrin **24** as an inseparable mixture with tetra(*tert*-butyl)phthalocyanine complex **25** (overall yield was 6.7%, 4 : 1 ratio). The authors performed the mixed condensation of *tert*-butyl-substituted isoindoline with malonic acid in the presence of zinc acetate at 360 °C under an inert atmosphere (Scheme 13). In addition to products **24** and **25**, a fraction composed of Zn complexes of (*tert*-butyl)tetrabenzoporphyrin (**26**) and tetra(*tert*-butyl)tetrabenzomonoazaporphyrin (**27**) was isolated from the reaction mixture. The demetallation of this fraction afforded a mixture of free-base ligands **28** and **29** (overall yield was 12%, 4 : 1 ratio). The products were separated into fractions by exploiting the difference in their solubility upon treatment with gaseous HCl in sulfuric acid at 0 °C. Under these conditions, Zn complexes **26** and **27** readily form the respective free macrocycles, whereas

Scheme 14



(*a*) HCl (gas), H_2SO_4

Scheme 15

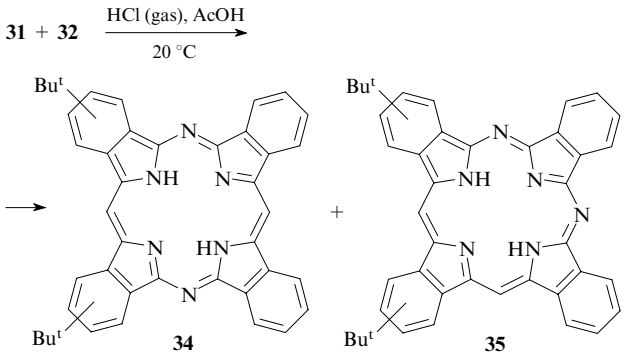


complexes **24** and **25** do not undergo demetallation (Scheme 14).

Zinc complex of di(*tert*-butyl)tetrabenzotriazaporphyrin **30** was synthesized starting from potassium 4-*tert*-butylphthalimide and malonic acid and was isolated in the individual state from a mixture with products **31**–**33** by chromatography on aluminium oxide (Scheme 15).[20] The yield of a mixture of isomeric complexes **31** and **32** was 2.9%.

Complex **30** was shown to be stable to gaseous hydrogen chloride in acetic acid at 20 °C.[20] Under these conditions, the corresponding free ligand is produced in an insignificant amount. The zinc complex with the phthalocyanine ligand shows a similar behaviour. By contrast, Zn complexes of *trans*- and *cis*-diazaporphyrins **31** and **32** form free macrocycles **34** and **35**, respectively. These isomers were isolated in the individual state by column chromatography on aluminium oxide (Scheme 16).

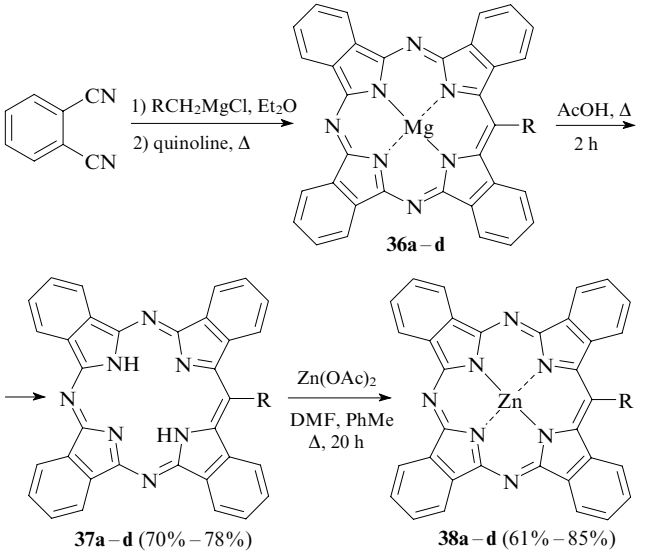
Scheme 16



An attempt to separate zinc complexes **31** and **32** by chromatography was unsuccessful.

To increase the solubility of tetrabenzotriazaporphyrin derivatives, Leznoff an co-workers[21] suggested also to introduce a substituent with a long hydrocarbon chain in position 27 of the macrocycle. The authors used a standard procedure based on the reaction of alkylmagnesium halides with unsubstituted phthalonitrile in diethyl ether at 20 °C followed by heating in quinoline at 120–185 °C for 18–24 h. Magnesium complexes **36a**–**d** thus obtained were sufficiently soluble to be purified by chromatography on silica gel before transformation to the free ligands. The

Scheme 17



R = n-C_5H_{11} (**a**), n-C_9H_{19} (**b**), n-$C_{13}H_{27}$ (**c**), n-$C_{17}H_{35}$ (**d**)

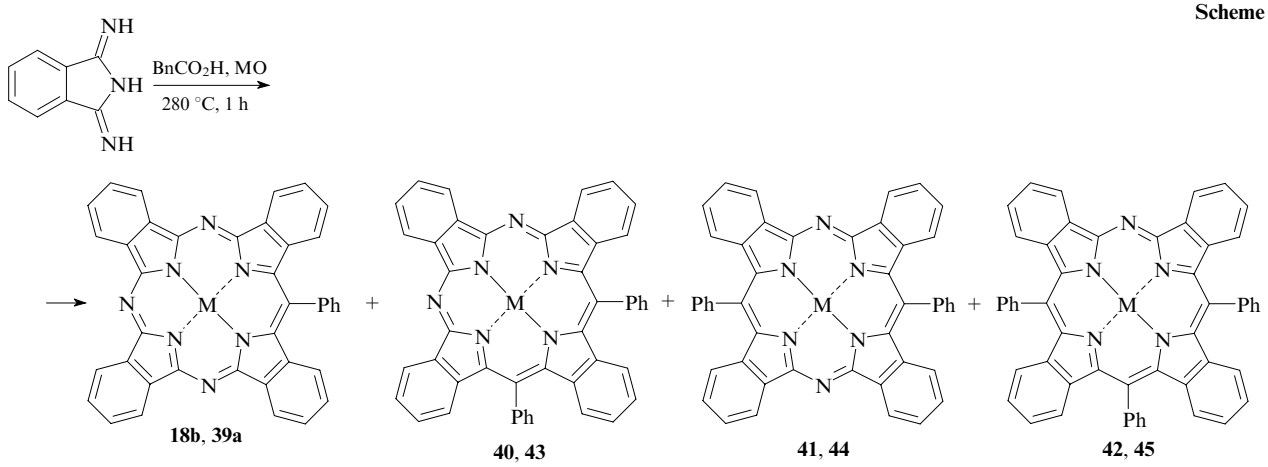
heating in acetic acid for 2 h resulted in the formation of 27-alkyltetrabenzotriazaporphyrins **37a**–**d**, which were recrystallized from toluene. The zinc complexes with these ligands (**38a**–**d**) were prepared by heating the corresponding macrocycles with a large excess of zinc acetate (10 equiv.) in a 1 : 1 dimethylformamide–toluene system (Scheme 17).

All zinc complexes can be easily recrystallized from diethyl ether. The introduction of an alkyl substituent in position 27 leads to an increase in the solubility of both free macrocycles and their metal complexes.

The template synthesis has also been widely applied in recent years for the synthesis of azaporphyrin derivatives. Galanin *et al.*[22,23] used 1,3-diiminoisoindoline, carboxylic acid containing a CH_2 group adjacent to the carboxy group and metal oxide (as the template agent) as the starting compounds. The yields of tetrabenzotriazaporphyrin derivatives **18a** and **39a** were 8.5% and 5%, respectively (Scheme 18). This approach was used to prepare other Mg (**40**–**42**) and Zn complexes (**43**–**45**) with 27-phenyl-substituted tetrabenzoazaporphyrins.

In addition to triazaporphyrins, this reaction gave complexes **40**–**45** as a difficult-to-separate mixture of products.

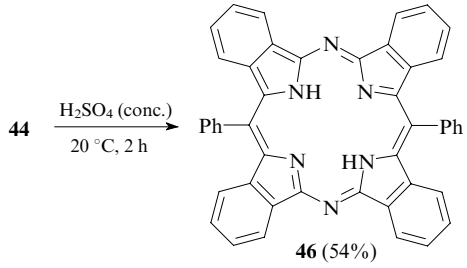
Scheme 18



M = Mg (**18b**, **40**–**42**), Zn (**39a**, **43**–**45**)

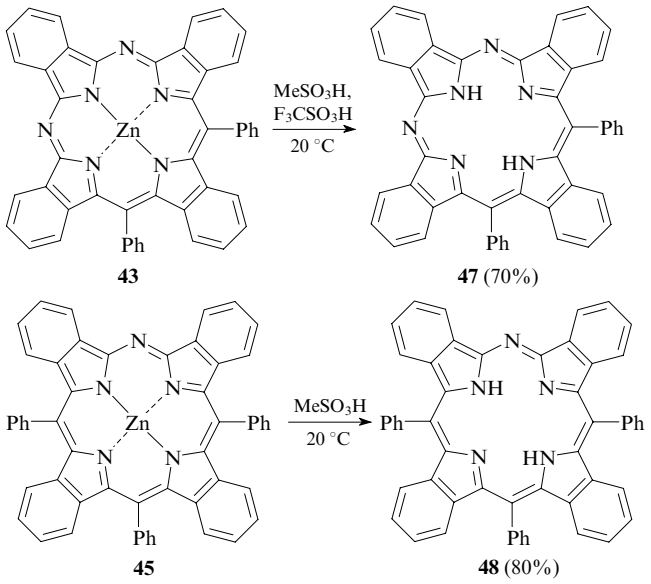
The zinc complexes with *cis*- (**43**) and *trans*-TBDAP (**44**) and TBMAP (**45**) can be demetallated with concentrated sulfuric acid at room temperature for 2 h to give target products in 62%, 54% and 73% yields, respectively. For example, free ligand **46** was produced from zinc complex **44** (Scheme 19).[23] It was noted that under these conditions, Zn complex of triazaporphyrin **18b** does not undergo demetallation, but instead it is subjected to sulfonation at higher temperatures or when the reaction is performed during a longer period of time.

Scheme 19



Borisov *et al.*[24] repeated this reaction using only zinc oxide as the template agent. These researchers obtained a similar mixture of products, which also contained the Zn complex of *meso*-tetraphenyltetrabenzoporphyrin. However, the yields in this reaction were very low (0.14% and 0.4% for compounds **43** and **45**, respectively), and the authors failed to increase the yields of the target products by varying the reactant ratio and the reaction temperature. Such low yields were attributed to the rapid formation of zinc phthalocyanine (in 10%–20% yield) from the starting 1,3-diiminoisoindoline. Two zinc derivatives (compounds **43** and **45**) were isolated and demetallated. The latter reaction was performed at room temperature using methanesulfonic acid or its mixture with trifluoromethanesulfonic acid (2 : 1), which are rarely employed in the chemistry of phthalocyanines.[24] The yields of free ligands **47** and **48** were 70% and 80%, respectively. It was reported that the reaction proceeds rapidly and is easily visually observed because the solution of the Zn complex rapidly changes the colour from dark green to dark red, due to protonation of the macrocycle (Scheme 20).

Scheme 20



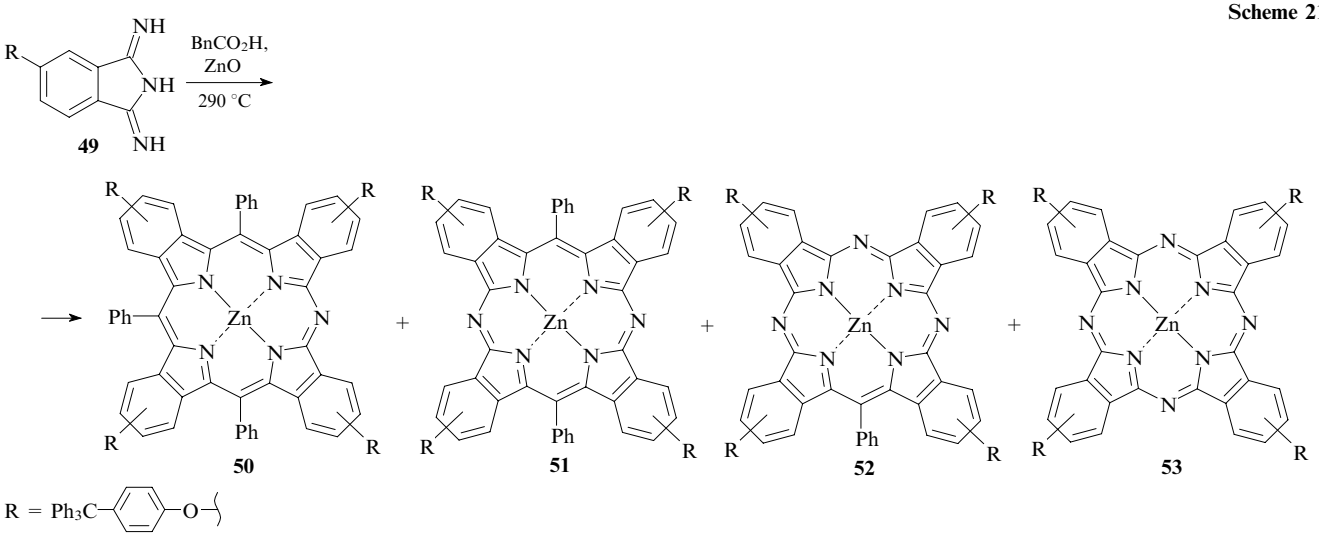
The zinc complex with phenyl-substituted tetrabenzotriazaporphyrin **39a** was also isolated from the reaction mixture; however, attempts to subject the latter compound to demetallation were unsuccessful due to its relative high stability.[24]

The template condensation was performed also with the use of isoindoline **49** containing the bulky 4-triphenylmethylphenoxy substituent.[25] The reaction of this compound with phenylacetic acid in the presence of zinc oxide afforded a mixture of products **50**–**53**, from which Zn derivative of TBTAP **52** was isolated in 12% yield (Scheme 21).

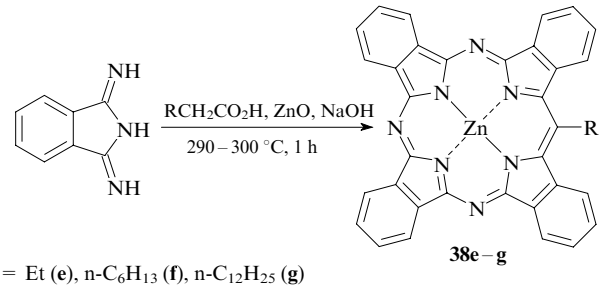
In contrast to the earlier studies,[22, 23] only one tetrabenzodiazaporphyrin, *viz*., *trans* isomer **51**, was found among the reaction products. The absence of the *cis* isomer was attributed to steric hindrance due to the presence of the bulky substituent.

Similar reactions of 1,3-diiminoisoindoline in the presence of zinc oxide as the template agent were performed also with other acids of the aliphatic series, such as butyric, caprylic and myristic.[26] These reactions produced Zn complexes **38e**–**g** (Scheme 22).

Scheme 21



Scheme 22



38e–g

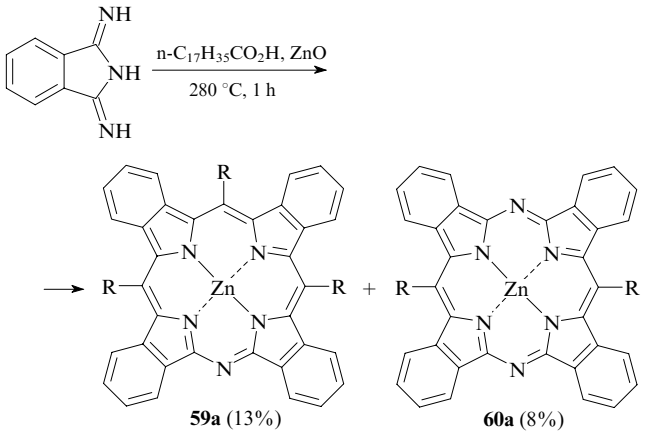
R = Et (**e**), n-C_6H_{13} (**f**), n-$C_{12}H_{25}$ (**g**)

The reactions were regioselective. In all cases, 27-alkyltetrabenzotriazaporphyrin was isolated as the only product. However, the reaction with the use of, for example, hexadecyloxyacetic acid under the same conditions produces a complex mixture of Zn compounds **54**–**58** containing different numbers of nitrogen atoms (from 0 to 3) in the *meso* positions of the macrocycle (Scheme 23).[27]

Bykova *et al.*[28] performed the reaction with the structurally similar reagent (stearic acid) in the presence of zinc oxide and isolated two reaction products, *viz.*, the Zn complexes of TBMAP (**59a**) and *trans*-TBDAP (**60a**) (Scheme 24).

A similar result was obtained in the reaction with caprinic acid.[29] Only derivatives of monoazaporphyrin (**59b**), *trans*- (**60b**) and *cis*-diazaporphyrins (**61**) were found as reaction products. These complexes were demetallated to the corresponding free macrocycles by treating with concentrated sulfuric acid at 20 °C (Scheme 25).

Scheme 24

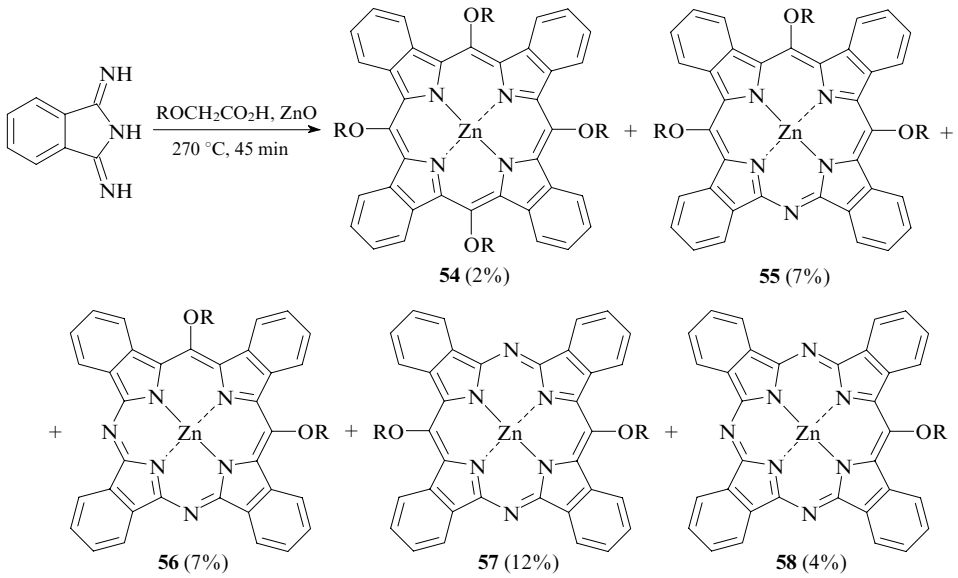


59a (13%) **60a** (8%)

R = n-$C_{16}H_{33}$

It should be noted that Zn complexes of 27-alkyltetrabenzotriazaporphyrin **38e**–**g**, unlike phenyl-substituted analogue **39a**,[23] form free ligands in high yields after the treatment with sulfuric acid at room temperature (Scheme 26).[26]

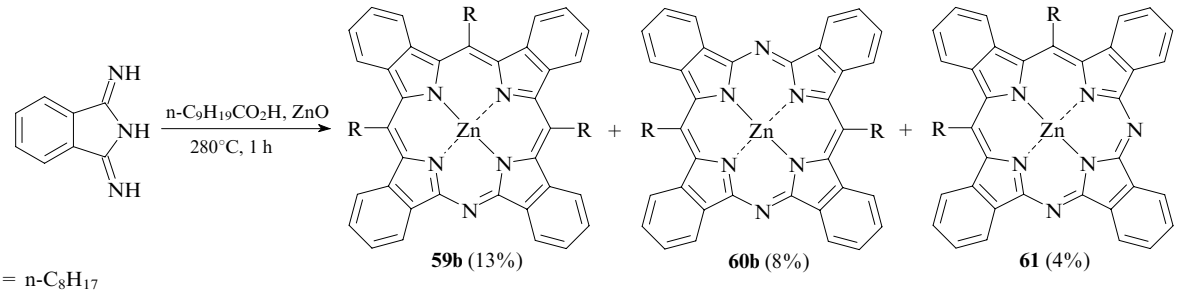
Scheme 23



54 (2%) **55** (7%) **56** (7%) **57** (12%) **58** (4%)

R = n-$C_{16}H_{33}$

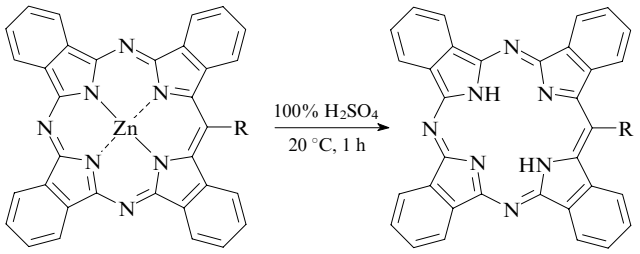
Scheme 25



59b (13%) **60b** (8%) **61** (4%)

R = n-C_8H_{17}

Scheme 26



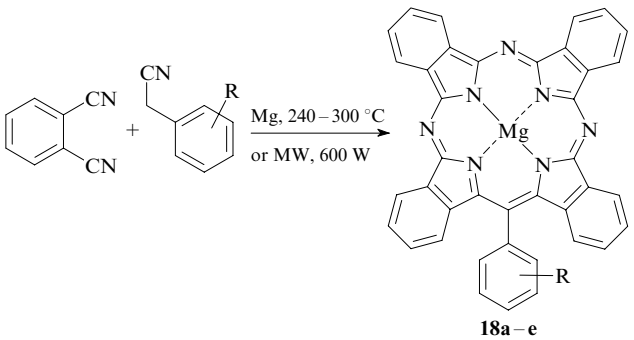
38e–g **37e–g** (82%–86%)

R = Et (**e**), n-C_6H_{13} (**f**), n-$C_{12}H_{25}$ (**g**)

The difficulty of demetallation of the zinc derivative of tetrabenzotriazaporphyrin was mentioned also by Borisov *et al.*[24]

We studied the mixed condensation of arylacetonitriles with unsubstituted phthalonitrile in the presence of magnesium powder.[30] The reaction proceeded upon slow heating from 240 to 300 °C and gave Mg complexes of 27-aryl-substituted tetrabenzotriazaporphyrins **18a–e**. Only magnesium phthalocyanine was isolated as a by-product. No impurities of diaza- and monoaza derivatives were found. This reaction made it possible to prepare magnesium complexes that are not available by other methods (Scheme 27).

Scheme 27

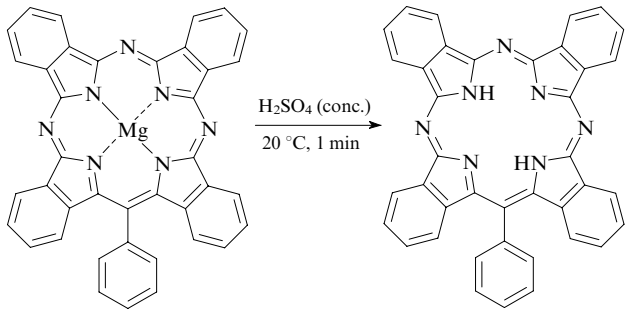


18a–e

R = 4-Me (**a**, yield 4%), H (**b**, 9%), 2-Me (**c**, 6%), 3-Me (**d**, 10%), 4-OMe (**e**, 3%)

The possibility of initiating this process by microwave radiation was shown by an example of the reaction of unsubstituted phenylacetonitrile. Magnesium complexes **18a–e** are convenient compounds for subsequent modifications. On the one hand, they are stable in air and can be subjected to chromatographic purification, unlike, for example, unstable dilithium derivatives. On the other hand, complexes **18** can be easily demetallated with sulfuric acid under mild conditions. This approach was used to prepare the corresponding free macrocycles, for instance, 27-phenyl-substituted TBTAP **19b** (Scheme 28), in nearly quantitative yields.[30]

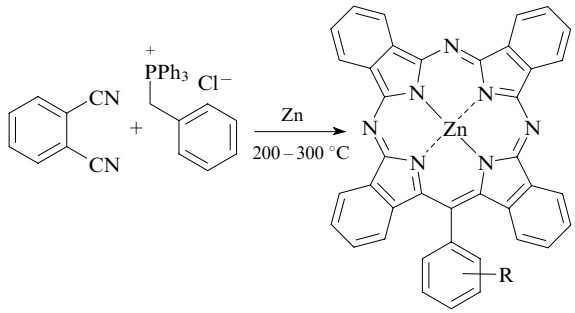
Scheme 28



18b **19b** (98%)

The heating of unsubstituted phthalonitrile and benzyltriphenylphosphonium salts as the synthetic equivalent of organomagnesium compounds in the presence of zinc dust in the temperature range of 200–300 °C afforded new zinc complexes **39a–e** with aryl-substituted tetrabenzotriazaporphyrin ligands.[31] These compounds are readily soluble in organic solvents and can be easily separated by column chromatography on silica gel (Scheme 29).

Scheme 29

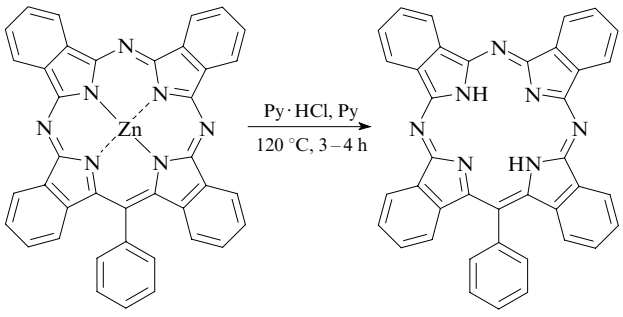


39a–e

R = H (**a**, 12%), 4-Me (**b**, 10%), 2-Me (**c**, 11%), 3-Me (**d**, 14%), 4-OMe (**e**, 2%)

As it was exemplified by phthalocyanines,[32] ions capable of being coordinated (for example, Zn^{II}) can have a substantial effect on the yield of the resulting metal complexes. Besides, it is difficult, if at all possible, to produce a free macrocycle from such metal complexes. Tetrabenzotriazaporphyrin complexes containing Zn(II) as the central ion exhibit similar behaviour. Many authors reported that they failed to demetallate Zn complex **39a**.[23, 24] We were the first to perform the quantitative demetallation of this compound under non-traditional conditions on heating in an ionic liquid (pyridinium hydrochloride, Py·HCl) (Scheme 30).[33]

Scheme 30

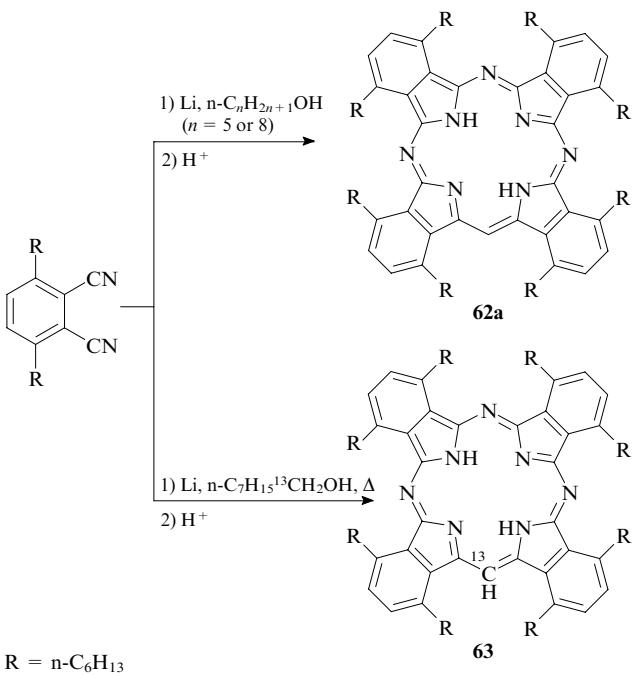


39a **19b** (96%)

Cammidge and co-workers [34, 35] studied the tetramerization of 3,6-di(n-hexyl)phthalonitrile in n-pentanol or n-octanol with metallic lithium and obtained, in addition to the corresponding phthalocyanine, a green by-product, *viz.*, 1,4,8,11,15,18,22,25-octa(n-hexyl)tetrabenzotriazapor-

phyrin (**62a**). The products were isolated in a ratio of 95 : 5 (Scheme 31).

Scheme 31



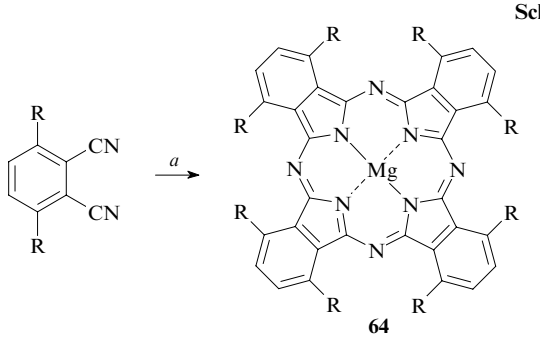
62a

63

It was noted that the reaction with the use of the lithium n-pentoxide prepared beforehand affords only octasubstituted phthalocyanine. An increase in the excess of lithium (from 2.1 to 19 equiv.) leads to a change in the phthalocyanine to tetrabenzotriazaporphyrin ratio to 77 : 23, and the use of n-octanol as a solvent with a higher boiling point compared to n-pentanol results in the 53 : 47 ratio. The study of the reaction in n-octanol ^{13}C isotope-labelled at the α position showed that the solvent (n-octanol) serves as a source of 87% of the *meso*-carbon atom in tetrabenzotriazaporphyrin **63**. It was also found that the composition of the reaction products depends on the substituents in the starting phthalonitrile. 3,6-Dimethyl-, 3,6-di(n-octyl)- and 3,6-di(n-decyl)phthalonitriles were shown to form mixtures of phthalocyanine and tetrabenzotriazaporphyrin, whereas 4-*tert*-butylphthalonitrile and 4,5-di(n-hexyl)phthalonitrile give only the corresponding phthalocyanines.[34]

A similar reaction was carried out with 3,6-di(n-hexyl)phthalonitrile in the presence of magnesium metal and magnesium acetate, as well as in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), instead of metallic lithium.[36] However, the heating of these reactants for 72 h resulted in the formation of only the corresponding Mg complex of octasubstituted phthalocyanine **64** in 14% yield, whereas TBTAP was not detected (Scheme 32).

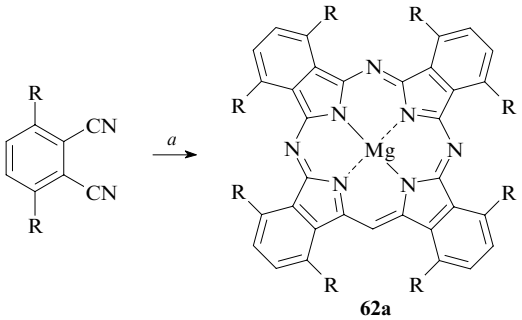
Scheme 32



64

Therefore, the tetramerization reaction of 3,6-dialkylphthalonitriles in the presence of metallic lithium in high-boiling alcohols giving phthalocyanine along with TBTAP derivatives, which was discovered in 2005,[34] showed the difference between phthalonitriles substituted at positions 3 and 6 of benzene rings and those containing no such substituents. Under these conditions, the latter compounds form exclusively phthalocyanines. However, it was found that this is not the only difference. In 2011, Cammidge *et al*.[36] studied the reaction of various organomagnesium compounds with 3,6-dihexylphthalonitrile giving tetrabenzotriazaporphyrins and isolated one and the same product **62a** with the unsubstituted methine bridge. The structure of this product does not depend on the Grignard reagent used (Scheme 33).

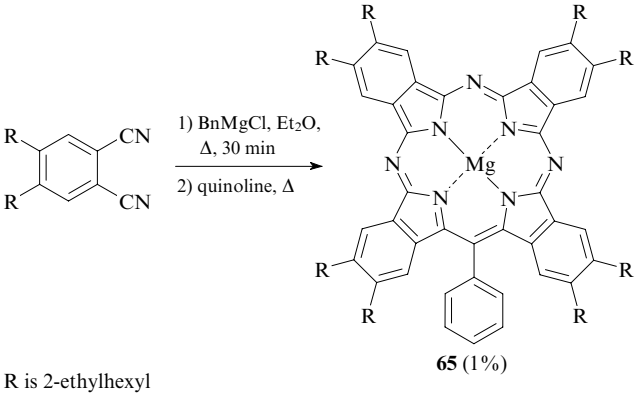
Scheme 33



62a

By contrast, the reaction of 4,5-bis(2-ethylhexyl)phthalonitrile with benzylmagnesium chloride performed under similar conditions produces substituted magnesium complex **65**.[36] The formation of a product containing the unsubstituted methine bridge was not observed (Scheme 34).

Scheme 34



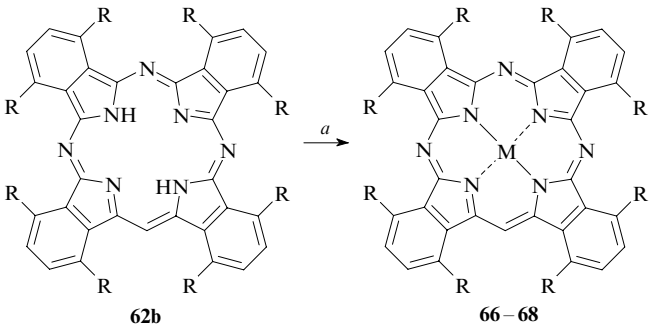
65 (1%)

This result is consistent with the data obtained by Leznoff and McKeown,[15] who studied the reactions of unsubstituted phthalonitrile, 4-neopenthyloxyphthalonitrile, 4-*tert*-butylphthalonitrile and 6-*tert*-butyl-2,3-dicyanonaphthalene with various organomagnesium reagents.

A similar scheme was applied to synthesize Mg complexes of octaoctyl-substituted TBTAP and related macrocycles, such as *cis*- and *trans*-TBDAP, TBMAP and TBP from 3,6-di(noctyl)phthalonitrile.[37] The demetallation on heating in acetic acid affords free ligands, which, in turn, form the corresponding copper complexes after heating with copper(II) acetate in n-pentanol.

In addition to the most well-studied Mg and Zn complexes with tetrabenzotriazaporphyrin, metal complexes of such ligands with other metal ions (for example, Ni, Pd, Cu and Fe) were also described. Since tetrabenzotriazaporphyrins are structurally similar to classical phthalocyanines, these compounds can be synthesized using methods developed for the preparation of phthalocyanines. For example, complexes **66**–**68** (Scheme 35) were synthesized by heating free ligand **62b** with an excess of metal acetate in pentyl alcohol.[36–38] After the chromatographic purification on silica gel, the metal complexes were obtained in yields up to 97%.

Scheme 35

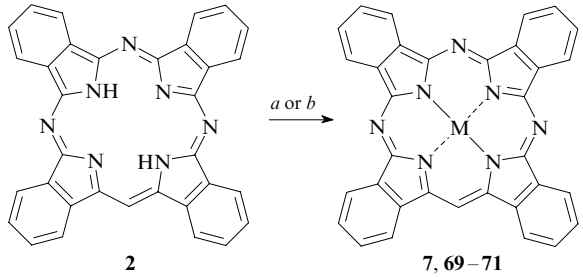


62b **66**–**68**

R = n-$C_{10}H_{21}$; M = Ni (**66**), Zn (**67**), Pd (**68**);
(*a*) $M(OAc)_2$, n-$C_5H_{11}OH$, Δ, 30 min

In the case of poorly soluble free ligands, such as unsubstituted tetrabenzotriazaporphyrin, dimethylformamide or pyridine can be used as the solvent.[39,40] One can refer to the synthesis of zinc complex **69** by the reaction of zinc acetate with free ligand **2**.[39] The reaction was performed by heating the reactants under reflux in DMF for 1 h. The metal complex precipitated after the dilution of the reaction mixture with an equal volume of water. The complexation of tetrabenzotriazaporphyrin with metals was carried out not only in higher alcohols but also in other high-boiling solvents, for example, in quinoline or 1-chloronaphthalene, in which the free ligand is readily soluble at high temperatures. This method was applied to prepare, with the use of metals (copper, zinc and magnesium), complexes **7**, **69** and **70**, respectively.[10] The synthesis of iron complex **71** was performed in the presence of iron(II) chloride as the source of the central ion. This reaction was brought to completion in 30 min (Scheme 36).

Scheme 36



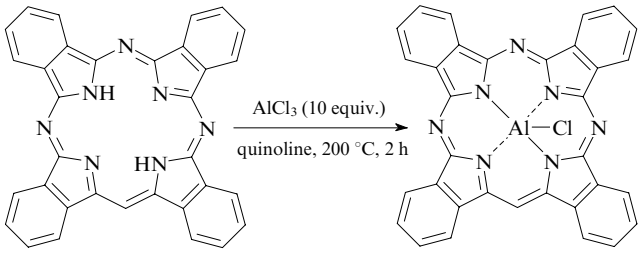
2 **7**, **69**–**71**

M = Cu (**7**), Zn (**69**), Mg (**70**), Fe (**71**);
(*a*) M, quinoline, Δ, 12 h (for M = Cu, Zn, Mg);
(*b*) $FeCl_2$, quinoline, Δ, 30 min (for M = Fe)

Metal complex **71** is readily soluble in quinoline, and it was isolated by diluting the reaction mixture with benzene followed by the addition of aqueous hydrochloric acid. Like iron phthalocyanine, compound **71** is soluble in aniline and forms the corresponding solvated complex.[10] Magnesium complex **70** is somewhat less soluble in quinoline. It should be noted that the synthesis of copper complex **7** in the presence of $CuCl_2$ is accompanied by chlorination of macrocyclic ligand **2** to form the corresponding monochloro derivative.[10]

Aluminium metal complex **72**, which was synthesized according to a similar scheme, proved to be readily soluble in quinoline.[41] The product was isolated by diluting the reaction mixture with a large amount of dichloromethane (Scheme 37).

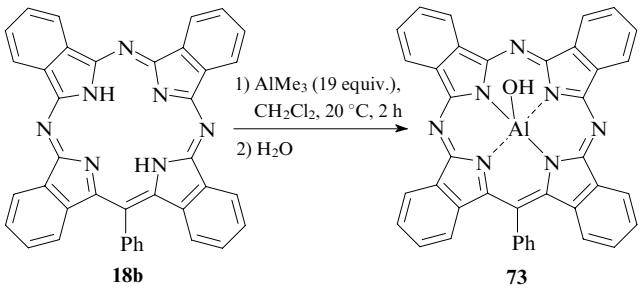
Scheme 37



2 **72**

In some cases, more basic reagents are employed. An example is the synthesis of aluminium complexes from 27-phenyltetrabenzotriazaporphyrin (**18b**).[42] Under these conditions, the reaction proceeds at room temperature. The yield of metal complex **73** is 68% (Scheme 38). The heating of compound **73** in chlorosulfonic acid at 150 °C for 2 h followed by the hydrolysis afforded the water-soluble sulfonated metal complex in 72% yield.[42]

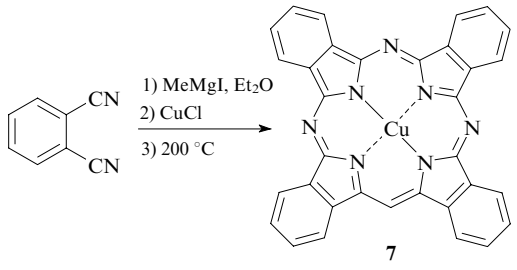
Scheme 38



18b **73**

A procedure for the synthesis of tetrabenzotriazaporphyrin complexes with metals other than magnesium was described.[10] According to this procedure, a salt of the required metal is introduced into the reaction after the addition of an organomagnesium reagent. For example, this approach was applied to prepare Cu complex **7** from phthalonitrile (Scheme 39). The mechanism of this transformation was not discussed in the original paper.

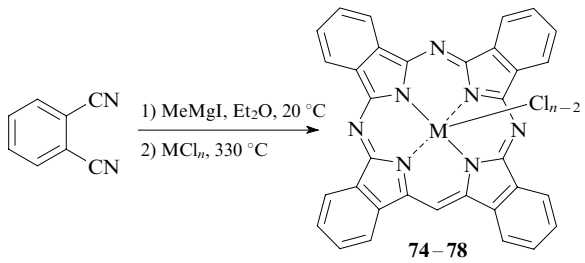
Scheme 39



7

Tetrabenzotriazaporphyrin complexes of chromium (**74**), manganese (**75**), vanadyl (**76**), cobalt (**77**) and iron(III) (**78**) were synthesized in a similar manner.[43, 44] In the latter case, the reaction was carried our in 1-chloronaphthalene (Scheme 40).

Scheme 40



74–78

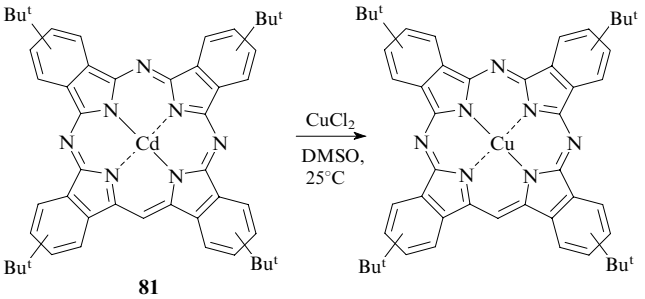
M = Cr^{3+} (**74**), Mn^{2+} (**75**), $(VO)^{2+}$ (**76**), Co^{2+} (**77**), Fe^{3+} (**78**); n = 2 or 3

It should be noted that attempts to use this approach for the preparation of sandwich-type complexes containing the tetrabenzotriazaporphyrin ligand were unsuccessful.[45]

We were the first to synthesize homo- and heteroleptic rare-earth double-decker complexes based on 27-phenyltetrabenzotriazaporphyrin (**19b**).[33] We prepared lutetium complex **79** according to a procedure developed by our research group for the selective synthesis of double-decker complexes with phthalocyanine ligands. The reaction of free ligand **19b** with lutetium acetylacetonate [$Lu(acac)_3$] proceeds on heating under reflux in hexadecyl alcohol in the presence of lithium methoxide to give green homoleptic complex **79** in good yield (81%) (Scheme 41). Heteroleptic complex **80** containing tetrabenzotriazaporphyrin and phthalocyanine ligands was generated under similar conditions with the participation of lutetium phthalocyanine. Macrocycle **19b** reacts with lutetium monophthalocyanine to form product **80** in 72% yield (see Scheme 41).

Cadmium complexes with TBTAP exhibit unusual properties. The addition of an excess of a copper or zinc salt to a solution of cadmium derivative **81** in dimethyl sulfoxide at 25 °C leads to transmetallation (Scheme 42),[46] whereas rather severe conditions are required for complexes of most of other metals.

Scheme 42

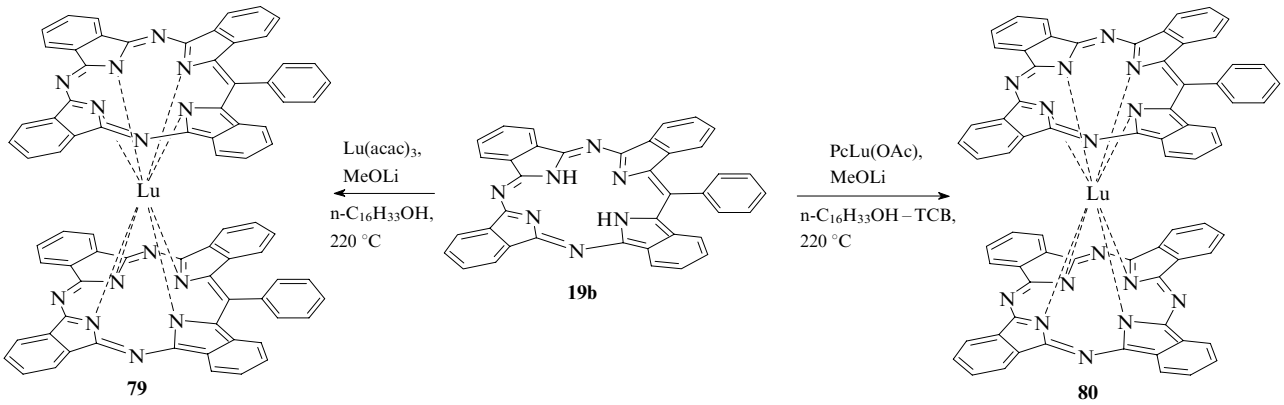


81

In reactions of phosphorus halides or oxohalides with free porphyrin-type ligands, the phosphorus atom can serve as a complex-forming agent. The reactions of ligands of the phthalocyanine series with trivalent phosphorus proceed in a different way than those with pentavalent phosphorus, and they can be used to synthesize a new macrocyclic system directly from phthalocyanine.[47] Thus, the reactions with pentavalent phosphorus compounds afford phthalocyanine derivative **82**, whereas the reactions with P^{III} compounds are accompanied by the ring contraction to form tetrabenzotriazacorrole derivative **83** (Scheme 43).

Antunes and Nyokong[48] studied the reactions of free tetrabenzotriazaporphyrin with trivalent and pentavalent phosphorus compounds. Both these reactions, unlike the reactions of phthalocyanines, give the same product, *viz*., phosphorus-containing tetrabenzotriazaporphyrin **84**. The dark-green product was isolated by chromatography on silica gel (yield 23%) (Scheme 44).

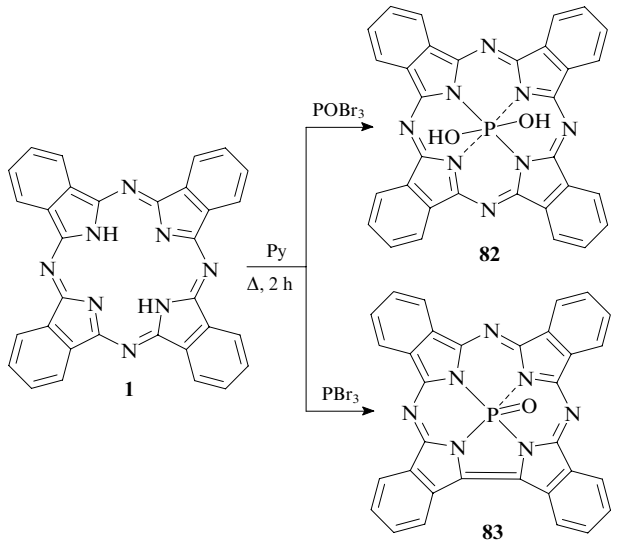
Scheme 41



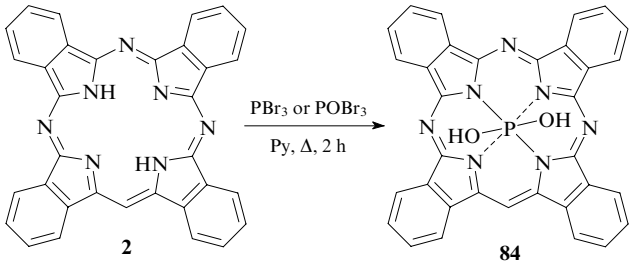
79 **19b** **80**

TCB is trichlorobenzene

Scheme 43



Scheme 44

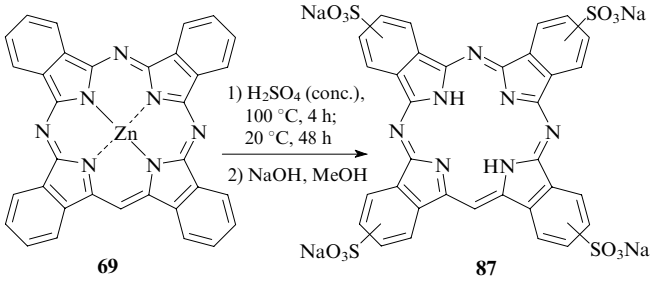


Silicon halides exhibit a similar behaviour. However, macrocyclic silicon dichloride **85** is very stable and is hydrolyzed to complex **86** only upon heating in pyridine in the presence of ammonium hydroxide for many hours (Scheme 45).[13, 14] A similar reaction produces a silicon complex from 27-phenyl-substituted tetrabenzotriazaporphyrin.

Free tetrabenzotriazaporphyrins and their complexes with metals are insoluble in water. However, for the practical application it is very important to prepare water-soluble derivatives. The main method used for imparting water solubility to TBTAP is based on the sulfonation of the macrocycle at benzene rings. The synthesis of first sulfonated derivatives of tetrabenzotriazaporphyrin was covered with a patent in 1938.[6] These compounds are produced by heating the Cu complex of TBTAP (**7**) in the presence of 5% oleum at 100 °C for 1 h. Macrocyclic sulfonic acid was isolated as the ammonium salt. However, the number of sulfo groups involved in the macrocycle is not reported in the patent.[6]

More recently, it was shown that concentrated sulfuric acid can be used as the sulfonating agent.[39] The reaction with Zn complex **69** also proceeds at 100 °C, but 4 h are required to bring this reaction to completion; the reaction time increases to 48 h if the reaction is carried out at 20 °C. This reaction produced tetrasulfonated compound **87** readily soluble in water. Compound **87** can be isolated as a green powder upon the addition of acetone to an aqueous solution of the mixture (Scheme 46).

Scheme 46

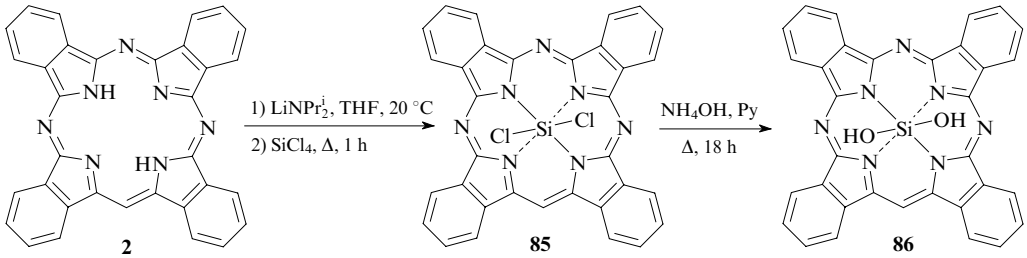


This reaction leads to the elimination of the zinc atom from the coordination sphere to form the free macrocycle. This is a rather unexpected result, because many authors mentioned the stability of Zn complexes to acids, including sulfuric acid.[19, 23, 24] Apparently, it is necessary to take into account the high temperature of the reaction and the long action of the corrosive reagent.

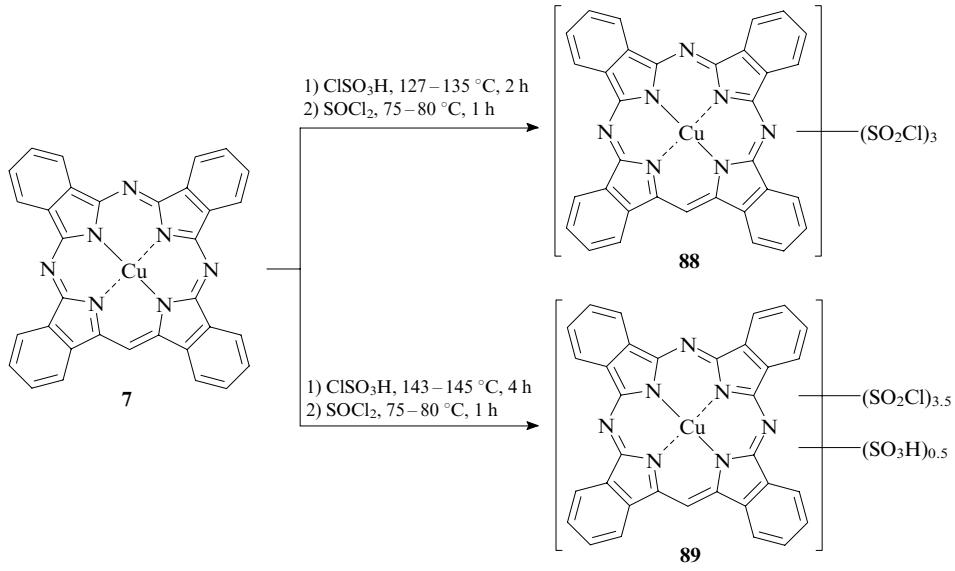
The sulfonation of the Cu complex of tetrabenzotriazaporphyrin (**7**) with chlorosulfonic acid was described in the patent.[49] It was noted that the reaction performed at 127–135 °C results in the introduction of three sulfonyl chloride groups per macrocycle **88**; at 143–145 °C, four sulfonyl chloride groups are introduced. The latter reaction is accompanied by partial hydrolysis of sulfonyl chloride groups because product **89** is isolated by the treatment of the reaction mixture with ice (Scheme 47). Macrocyclic sulfochlorides **88** and **89** were introduced into the reactions with various amines with the aim of preparing dyes.

The main difference between the structure of 27-aryl-substituted tetrabenzotriazaporphyrins and that of phthalocyanines is that the former compounds contain an additional aromatic ring, in which a sulfo group can also be introduced under particular conditions. It was found that the sulfonation of an aromatic substituent at position 27 takes place at lower temperatures (42–46 °C) compared to annulated benzene rings.[14] In this case, only the *meso*-aryl group is sulfonated, whereas the macrocycle remains intact. For example, this method was applied to synthesize *p*-tolyl

Scheme 45

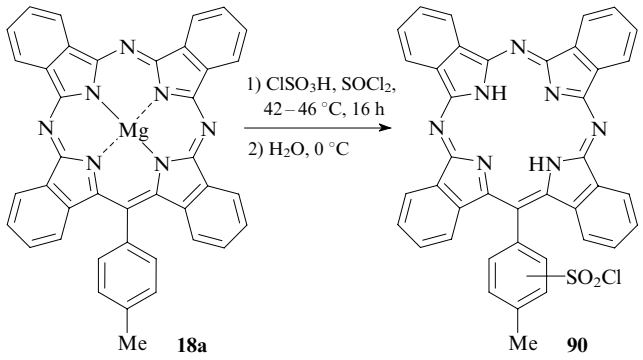


Scheme 47



derivative **90** containing the SO_2Cl group starting from Mg complex **18a** (Scheme 48).

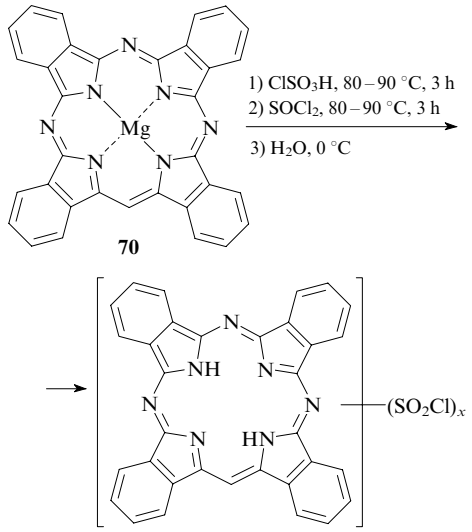
Scheme 48



The reaction is accompanied by the demetallation with a loss of the magnesium ion.

The sulfonation of the macrocyclic ligand with chlorosulfonic acid takes place at higher temperatures (80–90 °C), as was exemplified by unsubstituted magnesium tetrabenzotriazaporphyrinate **70** (Scheme 49).[14]

Scheme 49



III. Electronic absorption spectra of tetrabenzotriazaporphyrins and their complexes

As opposed to the symmetric phthalocyanine molecule (symmetry point group D_{4h}), tetrabenzotriazaporphyrins have lower symmetry (C_{2v}) due to the presence of the methine bridge instead of the nitrogen atom in the *meso* position. This is reflected in the spectral characteristics. The electronic absorption spectrum (EAS) of metallophthalocyanine shows one intense Q band. In the absorption spectra of tetrabenzotriazaporphyrins, the Q band is split into two components with similar intensities. In many studies, it was noted that the maxima of the most intense bands of phthalocyanine and the corresponding tetrabenzotriazaporphyrin are similar or coincide,[12,18] which interferes with the interpretation of the spectra. In the studies,[12,50] in which (TBTAP)Mg (**70**) was purified for the first time by column chromatography on aluminium oxide, the authors cast doubt on the purity and spectral characteristics of related complexes obtained in earlier works by crystallization. The close positions of the absorption maxima of phthalocyanine and the corresponding tetrabenzotriazaporphyrin often make it difficult to control the purification by column chromatography. The problem of the separation of *tert*-butyl-substituted tetrabenzotriazaporphyrin **22** and related phthalocyanine was considered by Karasev *et al.*[18] It was shown that the absorption maxima in the EAS of a tetrabenzotriazaporphyrin sample containing 15% of phthalocyanine are shifted only by 1 nm. It was concluded that the methods commonly used to check the purity by means of electronic spectroscopy do not provide reliable detection of even significant (up to 10%) impurities of phthalocyanine in tetrabenzotriazaporphyrin samples. We developed a procedure for chromatography on acid aluminium oxide, which made it possible to obtain the product containing less than 1% of *tert*-butylphthalocyanine.[18]

First spectra of chromatographically pure metal complexes of unsubstituted tetrabenzotriazaporphyrin (**70**) and its analogues — (TBDAP)Mg and (TBMAP)Mg — were published by a Belarusian research team (Fig. 1).[50] In the EAS presented in Fig. 1, the Q band of (TBTAP)Mg (**70**) is split into two components with similar intensities. The

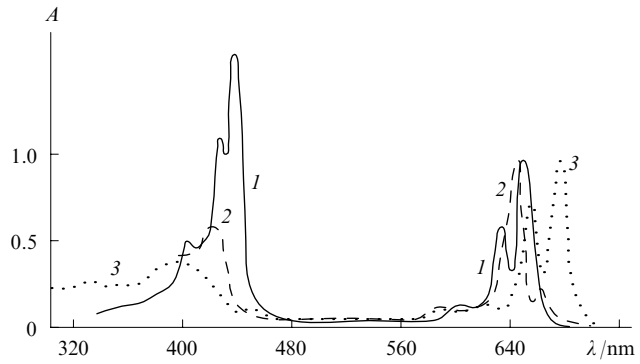


Figure 1. UV-Vis absorption spectra of Mg complexes in pyridine.[50]
(*1*) (TBMAP)Mg; (*2*) (TBDAP)Mg; (*3*) (TBTAP)Mg (**70**).

complex (TBMAP)Mg shows the tendency for the splitting of the Q band, whereas (TBDAP)Mg, to which the structure of the *trans* isomer was assigned, has only one slightly broadened Q band. More pronounced differences are observed in the UV region. Complex **70** has a broadened B band (Soret band) with a maximum at 395 nm and a small satellite. On the whole, the Soret band of this compound is similar to that of magnesium phthalocyanine and differs only by a slight long-wavelength shift. As compared with triazaporphyrin **70**, the Soret band of the diaza and monoaza analogues is characterized by a pronounced splitting into two components and a long-wavelength shift. Meanwhile, the intensity of the Soret band of (TBMAP)Mg increases and is higher than that of the Q band. A comparison of the absorption spectra of (TBTAP)Mg and PcMg shows that they are very similar. The main difference is that the Q band of complex **70** is split into two components, the maxima of the most intense bands of these two compounds coinciding. The regularities observed for the unsubstituted Mg complexes of TBTAP, TBDAP and TBMAP are also true for substituted analogues, including those containing a metalloid atom in the coordination sphere, for example, phosphorus derivatives **82**–**84** (Fig. 2).[48]

Recently, Cammidge and *et al.*[36] have synthesized a series of complexes of tetrabenzotriazaporphyrin and its analogues (TBDAP, TBMAP and TBP), as well as magnesium 1,4,8,11,15,18,22,25-octa(n-hexyl)phthalocyanine (**91**), and compared their spectral characteristics (Fig. 3).

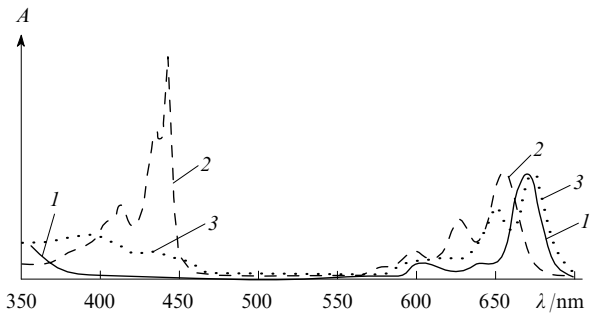


Figure 2. UV-Vis absorption spectra of phosphorus-containing complexes in DMSO.[48]
(*1*) Compound **82**; (*2*) compound **83**; (*3*) compound **84**.

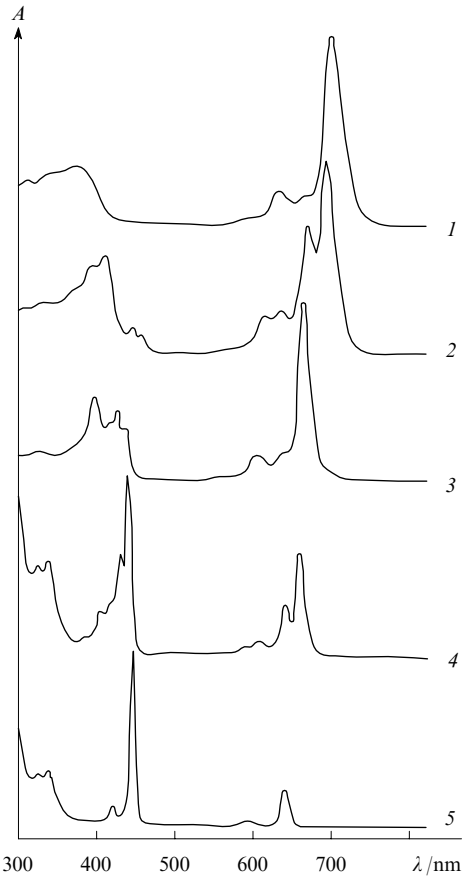
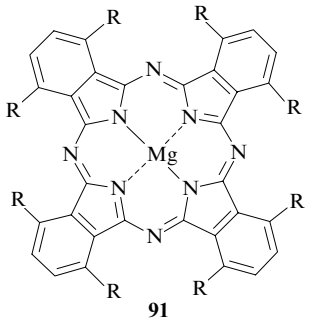


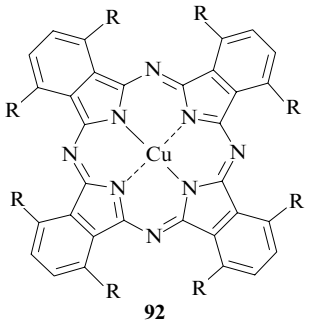
Figure 3. UV-Vis absorption spectra of Mg complexes in THF (λ_{max} are given in parentheses, nm).[36]
(*1*) Complex **91** (700); (*2*) (TBMAP)Mg (694, 671); (*3*) *cis*-(TBDAP)Mg (662, 403); (*4*) (TBMAP)Mg (659, 439, 429); (*5*) (TBP)Mg (641, 445).

In going from tetrabenzoporphyrin to phthalocyanine, the absorption maxima are shifted to longer wavelengths. This is consistent with the results of the earlier study[12] of unsubstituted cadmium complexes, where it was shown that an increase in the number of bridging nitrogen atoms in metal complex molecule causes long-wavelength shifts of absorption maxima in the visible region of the spectrum

Structures 91, 92



91



92

R = n-C_6H_{13}

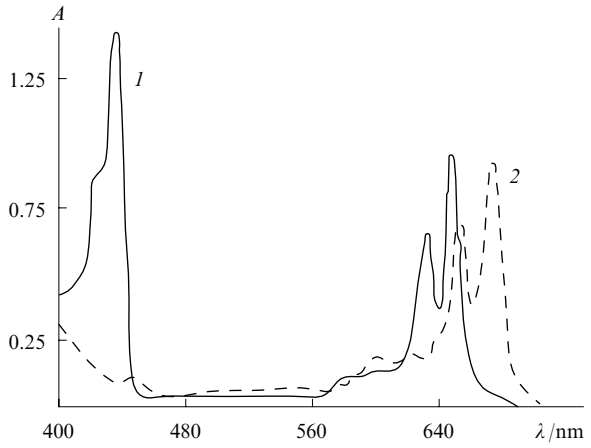


Figure 4. UV-Vis absorption spectra of the complexes (TBMAP)Cd (*1*) and (TBTAP)Cd (*2*) in pyridine.[12]

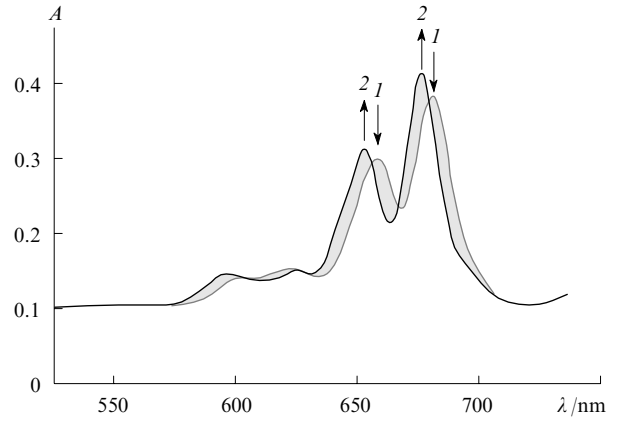


Figure 6. Changes in the UV-Vis absorption spectrum in the course of the metal exchange reaction in complex **81** with $CuCl_2$ in DMSO.
(*1*) In the initial instant of time; (*2*) after 40 min.[46]

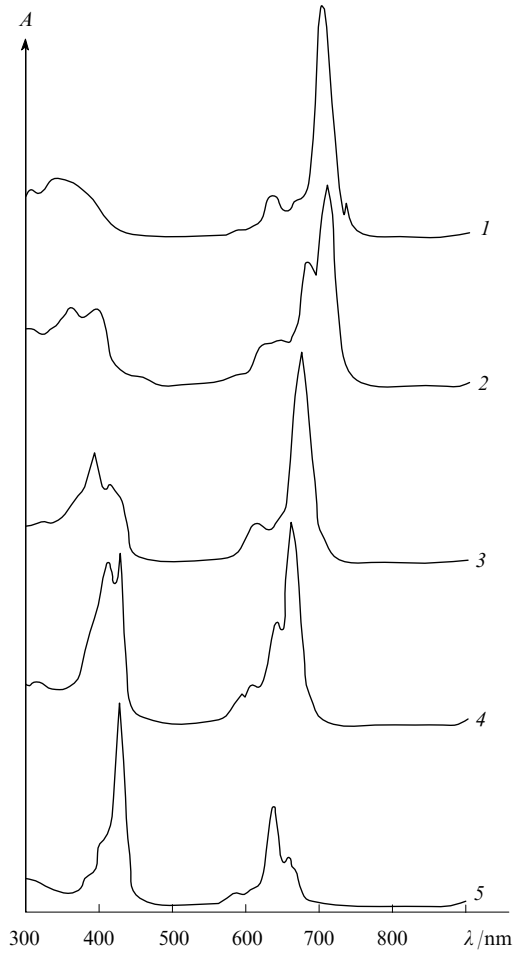


Figure 5. UV-Vis absorption spectra of Cu complexes in THF (λ_{max} are given in parentheses, nm).[36]
(*1*) Complex **92** (700); (*2*) (TBMAP)Cu (700, 675); (*3*) *cis*-(TBDAP)Cu (665, 391); (*4*) (TBMAP)Cu (661, 428, 412); (*5*) (TBP)Cu (637, 429).

(Fig. 4). Besides, the character of EAS strongly depends on the nature of the central metal ion. Thus, the general tendency for a long-wavelength shift is retained in going from magnesium to copper; only slight changes are observed in the character of the spectra and the positions of the maxima (see Figs 3 and 5). For comparison, Fig. 5 shows the spectrum of copper 1,4,8,11,15,18,22,25-octa-(n-hexyl)phthalocyanine (**92**).

The dependence of the spectral parameters on the metal ion in metal complexes was noted also by Solov'ev *et al.*[50] This property is at the heart of monitoring of the exchange reaction of the cadmium ion with the Cu^{II} ion in the Cd complex of tetra(*tert*-butyl)-substituted TBTAP (**81**).[46] The difference between the absorption maxima of two complexes is 5 nm, due to which the reaction can be monitored by EAS (Fig. 6).

In addition to planar metal complexes, we studied sandwich-type rare-earth complexes: homoleptic (**79**) and heteroleptic (**80**) complexes. The EAS study showed that these sandwich complexes, like related bis(phthalocyanine) complexes (for example, Pc_2Lu), are stable neutral π radicals. The main absorption bands in their spectra are split, which is typical also of planar tetrabenzotriazaporphyrins due to a lowering of the molecular symmetry, whereas the Q band in the spectrum of Pc_2Lu is not split (Fig. 7).

Complexes **79** and **80**, like diphthalocyanine complexes of rare-earth elements, have an important feature distinguishing them from planar complexes. Thus, they exhibit absorption in the near-IR region at 1200–1600 nm (see Fig. 7). The removal of the central metal ion from the tetrabenzotriazaporphyrin complex does not lead to a further complication of the absorption spectrum. The only change in the spectrum is an increase in the distance between the absorption maxima in the visible region, as was exemplified by magnesium complex **18b** and free ligand **19b** (Fig. 8).[30]

The EAS of free tetrabenzotriazaporphyrin ligand **2** prepared from the chromatographically pure magnesium complex was published in 1969.[50] As can be seen from Fig. 9, the pattern of the spectrum and the absorption maxima of unsubstituted ligand **2** are virtually identical to those of 27-phenyl-substituted analogue **19b** (see Fig. 8).

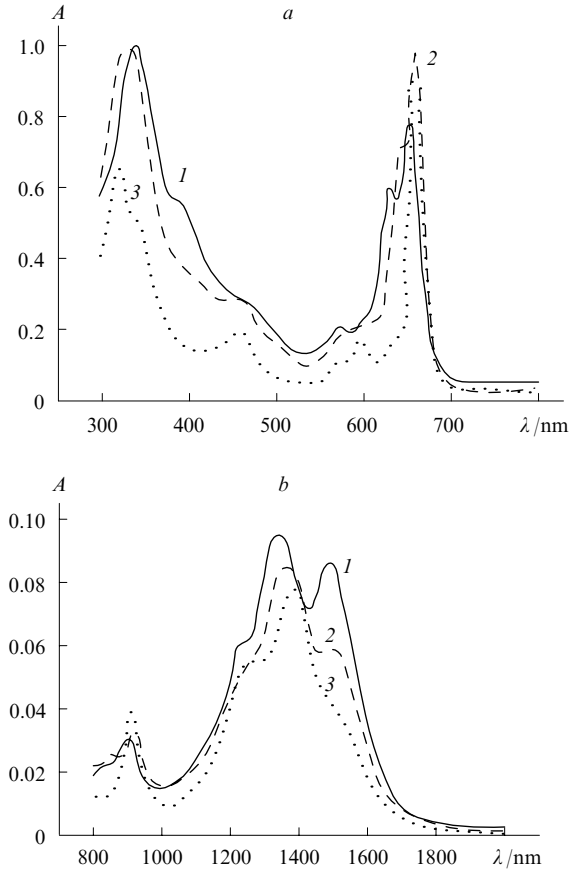


Figure 7. Electronic absorption spectra of sandwich complexes **79** (*1*), **80** (*2*) and Pc_2Lu (*3*) in CCl_4 in the visible (*a*) and near-IR regions (*b*).[33]

Figure 9 also shows the absorption spectrum of free tetrabenzomonoazaporphyrin ligand **5**. It can be noted that this spectrum is similar to the spectrum of (TBMAP)Mg,[50] but the Soret band region is more complicated.

The introduction of substituents both into the aromatic system of the macrocycle and in the *meso* position of the ring has only a slight effect on the character of the absorption spectrum. This can be seen by an example of

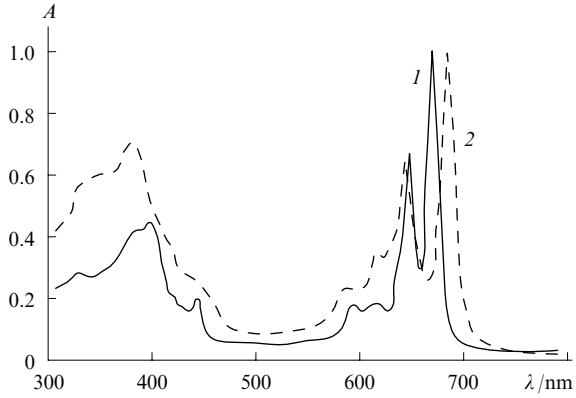


Figure 8. UV-Vis absorption spectra of magnesium complex **18b** (*1*) and the corresponding ligand **19b** (*2*) in THF.[30]

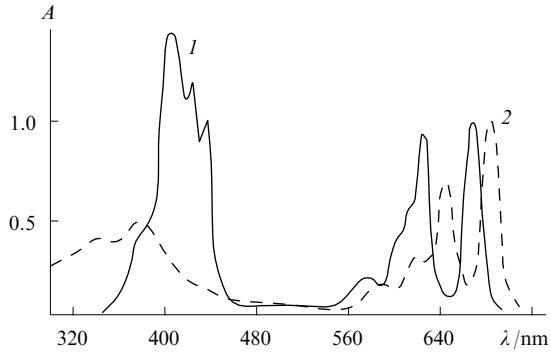


Figure 9. UV-Vis absorption spectra of free ligands **5** (*1*) and **2** (*2*) in pyridine.[50]

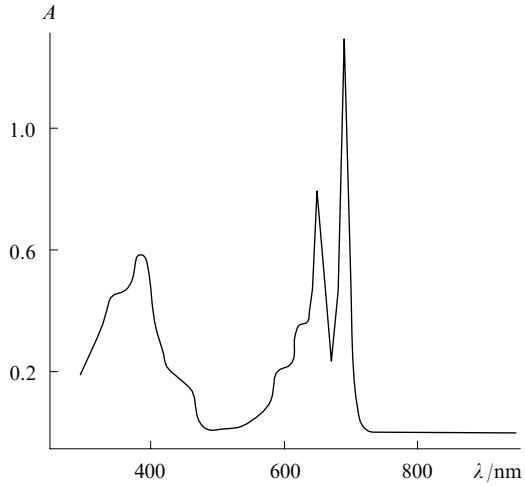
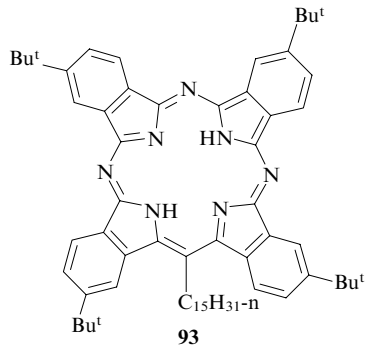


Figure 10. UV-Vis absorption spectrum of free ligand **93** in toluene.[51]

2,9,16,23-tetra(*tert*-butyl)-27-pentadecyltetrabenzotriazaporphyrin (**93**) (Fig. 10).[51] Van Lier and co-workers also noted that macrocycle **93** is stable as a film on glass on long-term exposure to air as compared with the sample freshly prepared in the study.[21]

Structure 93



93

The difference between the positions of the main maxima in the absorption spectra of the metal complex and the free ligand allows researchers to monitor the course of the complexation using absorption spectra. For example, this method was applied[45] to study the reaction of tetra(*tert*-

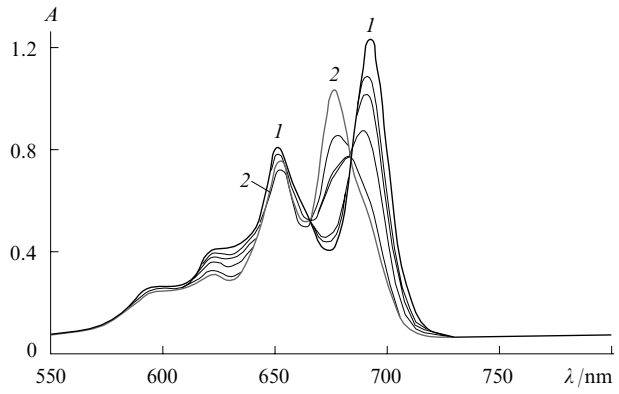


Figure 11. Changes in the UV-Vis absorption spectrum (thin lines) in the course of the complexation of ligand **22** with $CuCl_2$ in DMSO: (*1*) In the initial instant of time; (*2*) after 36 h.[45]

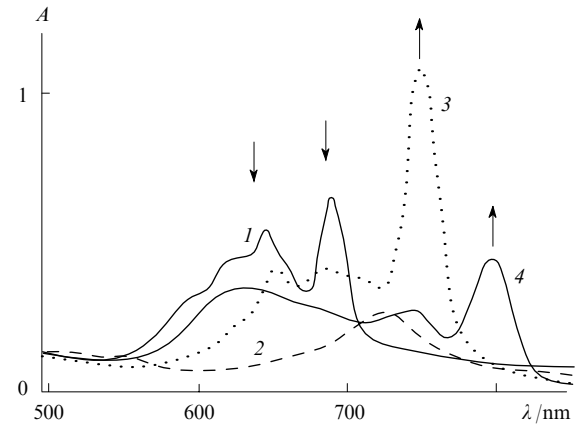


Figure 12. UV-Vis absorption spectra of neutral ligand **22** (*1*), its monoprotonated (*2*), doubly protonated (*3*) and triply protonated forms (*4*) in the ethanol–sulfuric acid system.[17]

butyl)-substituted ligand **22** with $CuCl_2$ in dimethyl sulfoxide (Fig. 11).

The tetrabenzotriazaporphyrin molecule has three *meso*-nitrogen atoms capable of being protonated in reactions with strong acids. This was detected by absorption spectroscopy. The protonation of tetra(*tert*-butyl)-substituted tetrabenzotriazaporphyrin **22** in ethanolic solutions of sulfuric acid (Fig. 12) was studied.[17]

Free tetrabenzotriazaporphyrin ligands have also acidic properties. The latter are manifested in that the reactions of these ligands with strong bases afford the corresponding mono- and dianions. The spectrophotometric titration of tetra(*tert*-butyl)-substituted ligand **22** in a DMSO–sodium cryptate system at room temperature was reported.[52] It was noted that the deprotonation occurs in two steps, each step being accompanied by strong changes in the absorption spectrum.

IV. Application of tetrabenzotriazaporphyrins and their complexes

The structural similarity of tetrabenzotriazaporphyrins and phthalocyanines manifests itself in the similarity of most of their physicochemical properties. This is why tetrabenzotriazaporphyrins are often used in the same fields as phthalocyanine derivatives. The first patent on the application of tetrabenzotriazaporphyrins[6] was granted one year after their discovery in 1937.[4] Due to one of the main features of this class of compounds, their deep blue or green colour, they were covered with a patent as dyes.[6] More recently, similar patents were issued on the use of analogues of these compounds containing various chromophore groups.[8,49] The needs of industry in compounds soluble in aqueous media gave rise to a class of water-soluble dyes — sulfo derivatives of tetrabenzotriazaporphyrins.[14,39,53] These derivatives have found use as fluorescent markers in biological assays.[13,14,41,42,54–69] Free tetrabenzotriazaporphyrins are employed in electron diffraction devices as light-sensitive layers.[70] The possibility of their application as sensors for gases was shown by an example of complexes of unsubstituted tetrabenzotriazaporphyrin with transition metals (chromium, iron, manganese, cobalt and vanadium).[44,71] Tetrabenzotriazaporphyrin complexes with iron and manganese can serve as catalysts for the oxidation of *o*-cresol by oxygen to salicylaldehyde.[72–74] Tetrabenzotriazaporphyrin derivatives are used also as optical data carriers.[75–78] In recent years, these macrocycles have found use in various electro-optic devices, including as materials for organic light-emitting diodes (OLED), which are main components of displays and other devices for imaging of information.[79,80]

V. Conclusion

To conclude, in the present review we summarize data on the synthesis and spectral characteristics of tetrabenzotriazaporphyrins and their complexes with metals obtained since their discovery (1937) and to the present time. Four approaches, which give products in comparable yields (5%–15%) and are approximately equally significant, can be distinguished among the above-considered synthetic methods. Each approach has its own advantages and drawbacks. One of these methods is rather well developed but includes two successive steps. The template synthesis based on 1,3-diiminoisoindoline is another approach. This is a one-step method, but it often simultaneously gives TBDAP and TBMAP complexes, which interferes with the isolation of target triaza derivatives. The third approach is based on the template synthesis with the use of arylacetonitriles. This is also a one-step method giving only TBTAP; however, the yield of target products substantially depends on the substituents in the starting arylacetonitrile. Finally, the template synthesis based on benzyltriphenylphosphonium salts affords tetrabenzotriazaporphyrin in one step; however, it is difficult to separate this product from triphenylphosphine and triphenylphosphine oxide that are present in the reaction mixture.

An increase in the number of publications on the synthesis and application of tetrabenzotriazaporphyrins in the past two decades is evidence that this is a promising field of investigation. The development of new methods for the synthesis of tetrabenzotriazaporphyrins and their complexes is an important problem since the synthetic approaches to such compounds are not well developed, while these compounds find ever increasing practical application in modern technologies.

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