Russian Chemical Reviews **80** (6) 531 – 551 (2011) © 2011 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2011v080n06ABEH004198

Subphthalocyanines and their analogues: methods for the synthesis and structure modification

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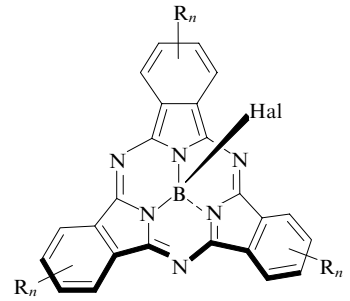
Abstract. Methods for the preparation and modification of mononuclear (A_3 and A_2B-types) and planar bi- and trinuclear subphthalocyanines are considered. Structural analogues of subphthalocyanines, *viz*., subazaporphyrins, are also discussed. The bibliography includes 83 references.

I. Introduction

In 1972, in an attempt to obtain boron phthalocyanine, German chemists Meller and Ossko [1] first discovered that self-cyclization of phthalonitrile in the presence of boron halides resulted in the formation of macrocyclic compounds strongly differing from phthalocyanines in their physicochemical properties. These compounds were named subphthalocyanines.

Subphthalocyanines (SubPc) are lower homologues of phthalocyanines. Their structure consists of three fused isoindole rings and a boron ion as a complex-forming centre.

Like phthalocyanines, subphthalocyanines exhibit strong absorption in the visible region (the absorption coefficient (ε) is $\sim$90 000 litre mol^{-1} cm^{-1}) and are chemically and thermally stable.[2, 3] Unique optical and electronic properties of these macrocycles due to the 14 π-electron conjugation system and also their unusual cone-shaped structure of C_3 symmetry (Fig. 1) attract researchers' attention.[1 – 69]



R = Alk, Hal, Alkenyl, *etc*.; Hal = F, Cl, Br, I.

By virtue of their specific structures, subphthalocyanines find application as materials for nonlinear optics, light emitting diodes, anion sensors, they are also used as molecular systems for energy transfer and represent the subjects of numerous studies in the supramolecular chem-

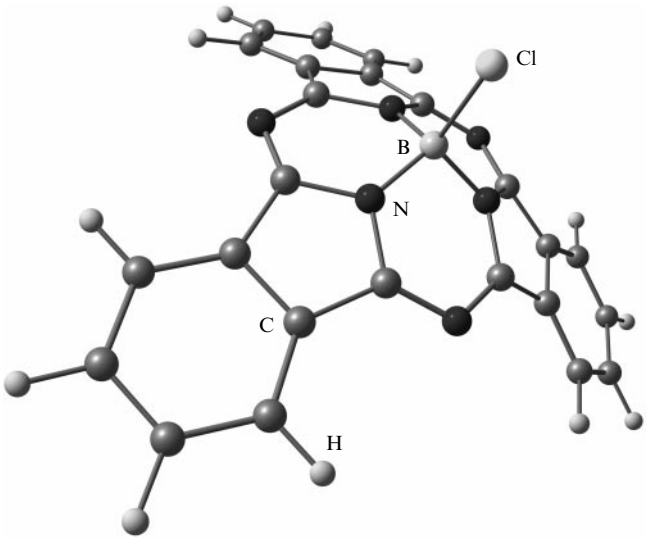


Figure 1. The optimized structure of subphthalocyanine (R_n = H, Hal = Cl) (the DFT calculations were carried out by the authors).

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Received 29 November 2010
Uspekhi Khimii **80** (6) 558 – 579 (2011); translated by S E Boganov

istry.[43, 67, 68, 70–72] High mobility of the axial halogen atom in subphthalocyanines enables easy modification of their structures and makes it possible to synthesize various heteroligand complexes, including those containing porphyrin or phthalocyanine ligands.[8, 73] Considerable efforts have been made to synthesize new derivatives of these unique compounds since their discovery.[4, 16, 20, 66, 67]

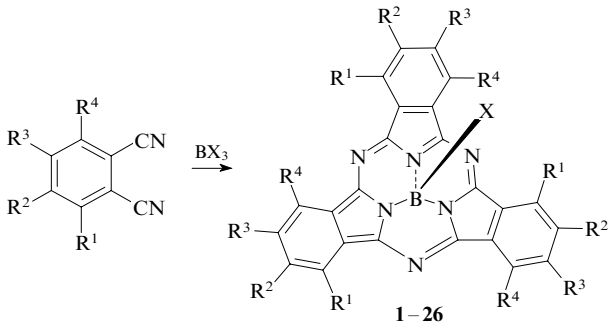
The present review is devoted to methods for the synthesis of subphthalocyanines of both symmetric and nonsymmetric structure and subazaporphyrins, the closest structural analogues of subphthalocyanines. A special section deals with methods of structural modification of subphthalocyanines, including processes proceeding not only with preservation of the number of π-electrons but also with expansion of the subphthalocyanine macrocycle.

II. Methods for the synthesis of subphthalocyanines and their analogues

Subphthalocyanines are formed by trimerization of phthalonitriles (phthalogens) under the action of boron derivatives, preferably boron halides (Refs 4, 10, 18, 27, 35, 44, 45, 48, 51–54, 58, 62, 64, 68). When one phthalogen is used, phthalocyanines with the composition A_3 are formed, whereas the use of a mixture of phthalonitriles in the cyclization opens the way to the synthesis of unsymmetrically substituted subphthalocyanines of the A_2B type, as well as of their bi- and trinuclear analogues.

1. Self-cyclization of phthalonitriles

The reaction of phthalogens with boron halides is usually carried out in naphthalene or in α-chloronaphthalene at *ca.* 200 °C resulting in subphthalocyanines **1**–**26** (Table 1).



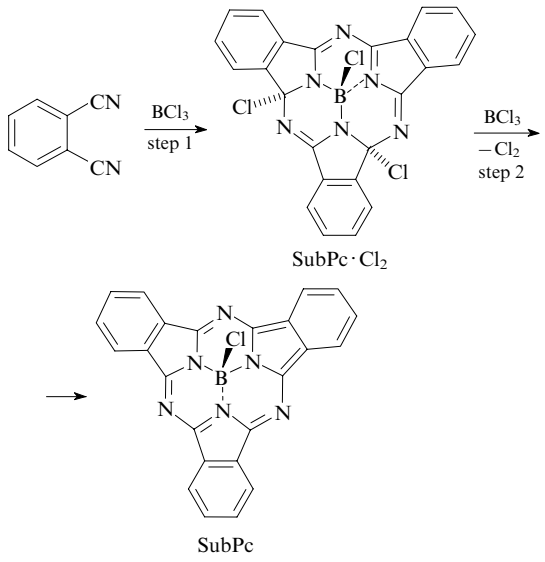
1–**26**

The process proceeds in two steps, this can be illustrated, for example, by considering the reaction of phthalonitrile with BCl_3. An associate, a donor–acceptor complex, is formed initially. On heating, it produces the intermediate compound $SubPc \cdot Cl_2$ (step 1). According to quantum chemical calculations (DFT//B3LYP/6-31G*), the macrocycle in this compound is distorted, and this intermediate, being unstable, readily transforms into the final product.[74]

Table 1. Yields of boron-containing subphthalocyanines **1**–**26**.

Compound	R^1–R^4	X	Yield (%)	Ref.	Compound	R^1–R^4	X	Yield (%)	Ref.
1	$R^1 = R^4 = H$, $R^2/R^3 = SO_2Cl/H$ [a]	Br	60	23	**13**	$R^1 = R^2 = H$, $R^3/R^4 = SO_2Pr^n/H$	Cl	15	58
2	$R^1 = R^4 = H$, $R^2/R^3 = NO_2/H$	Br	77	53	**14**	$R^1 = R^4 = H$, $R^2/R^3 = NO_2/H$	Cl	88	62
3	$R^1 = R^4 = H$, $R^2/R^3 = OC_5H_{11}$-neo/H	Br	23	53	**15**	$R^1 = R^4 = H$, $R^2/R^3 = I/H$	Cl	70	62
4	$R^1 = R^4 = H$, $R^2/R^3 = OPr^i/H$	Br	19	53	**16**	$R^1 = R^2 = R^3 = R^4 = H$	Cl	85	62
					17	$R^1 = R^2 = R^3 = R^4 = F$	Cl	74	62, 69
5	$R^1/R^4 = OPr^i/H$, $R^2 = R^3 = H$	Br	13	53	**18**	$R^1 = R^4 = H$, $R^2 = R^3 = SC_8H_{17}$-n	Cl	51	62
6	$R^1/R^4 = OC_5H_{11}$-n/H, $R^2 = R^3 = H$	Br	19	31	**19**	$R^1 = R^4 = H$, $R^2 = R^3 = SO_2C_8H_{17}$-n	Cl	64	62
7	$R^1 = R^4 = H$, $R^2/R^3 = Me/H$	Cl	60	44	**20**	$R^1 = R^4 = H$, $R^2 = R^3 = OMe$	Cl	21	64
8	$R^1 = R^4 = H$, $R^2/R^3 = Bu^t/H$	Cl	58	44	**21**	$R^1 = R^4 = H$, $R^2 = R^3 = Bu^n$	Cl	88	75
9	$R^1 = R^4 = H$, $R^2/R^3 = SC_6H_4Me$-4/H	Cl	13 (C_3) + + 35 (C_1) [b]	45	**22**	$R^1 = R^2 = R^3 = R^4 = H$	F	20	1
					23	$R^1 = R^2 = R^3 = R^4 = H$	Ph	10	4
10	$R^1/R^2 = SC_6H_4Me$-4/H, $R^3 = R^4 = H$	Cl	11 (C_3) + + 3 (C_1) [b]	45	**24**	$R^1 = R^4 = H$, $R^2 = R^3 = Me$	Ph	3	2
11	$R^1 = R^4 = H$, $R^2/R^3 = OPy$-2/H	Cl	19	52	**25**	$R^1 = R^4 = H$, $R^2 = R^3 = n$-C_5H_{11}	Ph	5	2
12	$R^1 = R^2 = H$, $R^3/R^4 = SPr^n/H$	Cl	1	58	**26**	$R^1 = R^2 = R^3 = R^4 = H$	Bu^n	1	2

[a] Hereinafter, the character / ('slash') denotes a pair of interchangeable substituents; [b] the symmetry of the complex is shown in parentheses (see Section III).



The second step of the formation of subphthalocyanines can be regarded as the combination of two reactions, *viz*., elimination of the chloride anion followed by spontaneous detachment of the cation Cl^+:

$$SubPc \cdot Cl_2 + BCl_3 \longrightarrow$$

$$\longrightarrow SubPc \cdot Cl^+ + BCl_4^- \ (\Delta H = 59.1 \text{ kcal mol}^{-1}), \quad (1)$$

$$SubPc \cdot Cl^+ + BCl_4^- \longrightarrow$$

$$\longrightarrow SubPc + Cl_2 + BCl_3 \ (\Delta H = -71.3 \text{ kcal mol}^{-1}). \quad (2)$$

Hence, BCl_3 acts as a catalyst in the second step rather than as a reagent. This assumption was confirmed experimentally by carrying out trimerization of phthalonitrile under the action of BCl_3 at different reactant ratios.[74]

The yields of the target subphthalocyanines are strongly influenced by the nature of boron-containing reagents, their reactivity with respect to phthalonitriles increases in the series $BAlk_2Br < BPh_3 < BF_3 < BCl_3 < BBr_3$. However, the choice of the reagent is also associated with the stability of the intermediate complex formed.

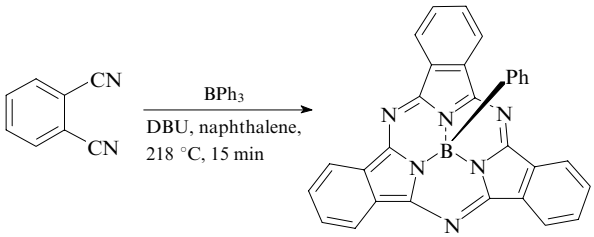
Boron tribromide readily reacts with phthalonitriles with formation of compounds **1**–**6** in 20%–60% yields.[23, 53] This reagent is commercially available and is usually utilized as a 1 M solution in heptane or dichloromethane. However, subphthalocyanines with the axial bromine atom were shown to be insufficiently stable. In addition, the bromine atom is prone to nucleophilic substitution and this complicates chromatographic purification of such complexes.

The number of works where BCl_3 has been used for the synthesis of subphthalocyanines is larger than those where other boron derivatives were utilized. Like BBr_3, boron trichloride is commercially available and is used as a 1 M solution in hexane or a 10% solution in dichloromethane. The yields of the target products **7**–**21** reach sometimes 80%, but generally they depend on the type of substituents in the phthalogen.[44, 45, 52, 58, 62, 64] Using BCl_3 as a complex-forming reagent, one should pay special attention to the choice of a solvent. It was found that higher temperature is needed in the case of less reactive phthalogens; therefore the process is carried out in a high-boiling solvent. However, the published data do not allow inferring unequivocal correlation between the reactivity and the nature of substituents in the phthalonitrile.

Chlorosubphthalocyanines are stable in the solid state, but in solutions, especially under light, they decompose in several days. Their relative stability depends on the type of peripheral substituents. Particularly, triiodosubphthalocyanine **15** is more stable[62] than its analogues with other substituents. It is also worth noting that chlorine-containing subphthalocyanines are more stable to anionic reagents than the corresponding bromo analogues, this allows application of chromatographic methods for their purification.

Boron trifluoride is a reagent that is rarely used for the synthesis of subphthalocyanines because of its low reactivity. At the same time, subphthalocyanine **22** is more stable than the corresponding bromo and chloro analogues.[69]

Owing to the high reactivity of boron halides, synthesis is often accompanied by side processes. After completion of the reactions, electrophilic substitution products were detected in the reaction mixtures by HPLC in addition to the target macrocyclic compounds.[2] Halogenation of peripheral substituents can be avoided by introducing electron-withdrawing substituents into the aromatic system[62] or by using BPh_3 instead of boron halides.[4] For example, trimerization of 4-nitrophthalonitrile in the presence of BBr_3 and BCl_3 affords complexes **2** and **14** in 77% and 88% yields, respectively. Lower reactivity of BPh_3 resulting in smaller yields of the target subphthalocyanines should be taken into account.[2, 4] Subphthalocyanine **23** was prepared in low yield in the reaction of unsubstituted phthalonitrile with BPh_3 in naphthalene under rather drastic conditions in the presence of a stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[4]



23

No side products of peripheral halogenation formed, which made it possible[4] to grow crystals of **23** suitable for X-ray diffraction study (Fig. 2). A characteristic feature of the structure of phenyl-substituted subphthalocyanine is that its planarity is distorted and the system acquires the saucer shape due to coordination of the boron atom. It was found that the presence of the axial phenyl substituent increases solubility of the complex and facilitates its chromatographic purification. Distorted geometry is also typical of subphthalocyanines with other axial substituents.[3, 5, 7]

Later salt $Bu^n_4N^+BPh_4^-$ was used for the preparation of compound **23**.[69] The increase in the nucleophilicity of the reagent resulted in only small increase in the yield of the target product; however, this made it possible to carry out the reaction under mild conditions.

It is noteworthy that trimerization of dialkyl-substituted phthalogens under the action of BPh_3 does not give phenylsubphthalocyanines. Compounds **24** and **25** could only be obtained[2] in the presence of a superbase, [1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)]phosphoranylidenamino]-2l^5,4l^5-*catena*-diphosphazine] (P_4-Bu^t).[76]

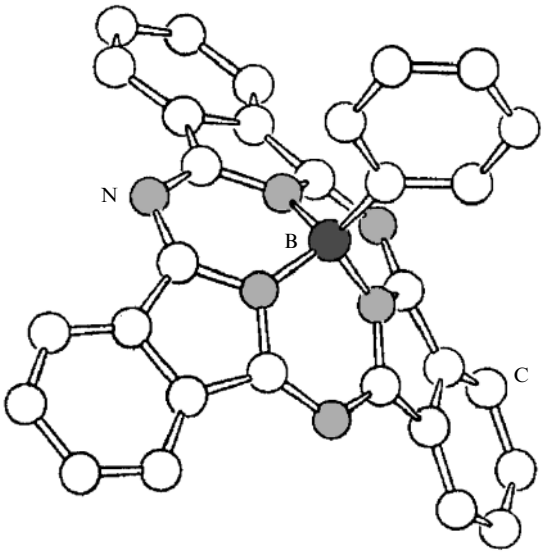
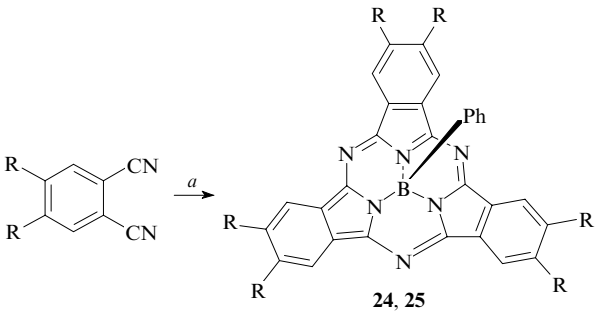


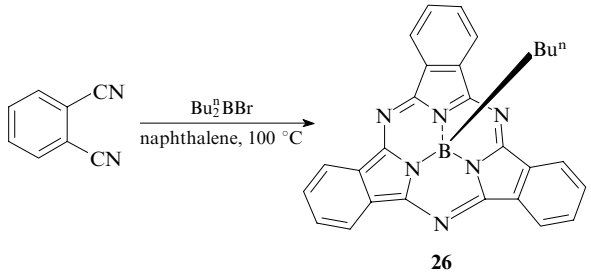
Figure 2. The crystal structure of compound **23** (H atoms are omitted for simplicity).[4]



R = Me (**24**), n-C_5H_{11} (**25**); (*a*) BPh_3, P_4-Bu^t, naphthalene, 190 °C, 12 h.

An attempt of synthesis of subphthalocyanines **24** and **25** from 1,3-diiminoisoindolines and BPh_3 has been undertaken.[2] However, this approach is not universal and thus not suitable for every boron-containing reagent.

Trialkylboranes do not give the trimerization products of phthalonitriles even in the presence of an excess of DBU. To obtain subphthalocyanine **26**, Geyer *et al.*[2] used the mixed reagent, Bu^n_2BBr, in the reaction.



The process starts only at 100 °C, whereas decomposition of the target complex occurs above 120 °C. Chromatographic purification of axially substituted butylsubphthalocyanine is extremely laborious, therefore the yield of compound **26** did not exceed 1%.

Mixed boron halides represent a class of important reagents for the synthesis of subphthalocyanines. The above-mentioned problem of peripheral halogenation upon formation of the subphthalocyanine macrocycle can be solved not only by reducing the basicity of the macrocyclic π-system or suppressing activity of the complex-forming agent, but also by decreasing the number of halogen atoms in the latter. Indeed, in the case of mixed boron-containing reagents like Ph_2BBr, Bu^nBBr_2, $PhBCl_2$, both the phenyl and alkyl substituents, being poor leaving groups, occupy the axial position of the subphthalocyanine macrocycle, while the halide ions undergo elimination without affecting the macrocycle periphery.[20] Nevertheless, such a replacement of the reagents does not result in an increase in the yields of the target products.

In our opinion, main attention should be paid to the investigation of the process of formation of the intermediate complexes of phthalonitrile with BX_3 and factors that determine their stability. These complexes are donor–acceptor compounds where the CN groups of phthalonitrile play the role of bases and BX_3 acts as an acid. We found that preliminary isolation of such a complex and its subsequent fast heating to 180 °C in *o*-dichlorobenzene (DCB) make it possible to obtain subphthalocyanines in approximately 90% yields without competitive formation of the peripheral halogenation by-products.[75] At the same time, slow heating results in decomposition of the complex, and subphthalocyanine thus formed contains halogenation products as an admixture.

The intramolecular 14 π-electron conjugation system is responsible for the appearance of intense absorption band of subphthalocyanines in the visible region (Fig. 3).[2] The electronic absorption spectra of subphthalocyanines only slightly differ from the spectra of their phthalocyanine analogues, the major difference being the hypsochromic shift of the Q-band by approximately 100 nm.[75] Subphthalocyanines are of intense purple colour and well soluble in moderately polar organic solvents. Alkyl groups as axial or donating peripheral substituents increase solubility of the complexes in hexane and petroleum ether.[1,2] In contrast to phthalocyanines, subphthalocyanines do not aggregate in solutions at concentrations up to 10^{-1} mol litre^{-1}, this makes it possible to use NMR spectroscopy for the study of their structures.

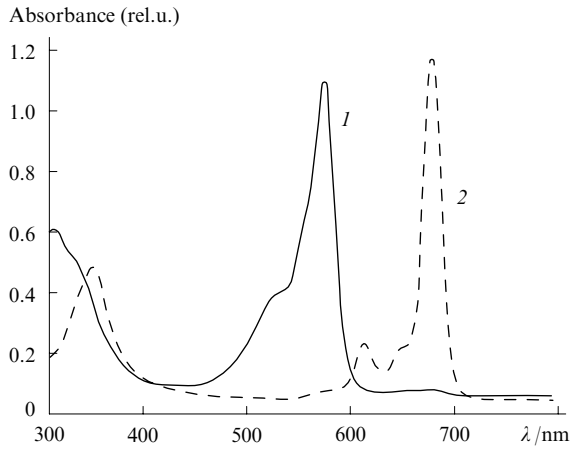
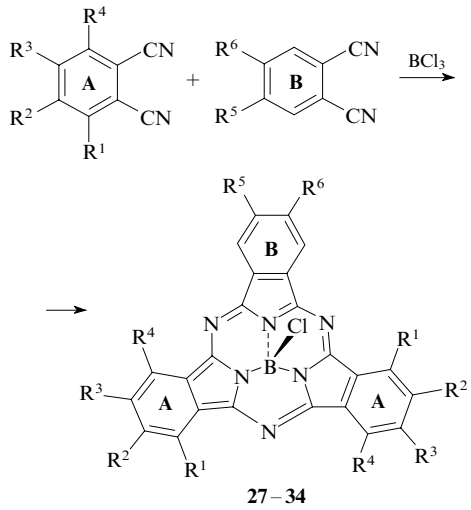


Figure 3. Electronic absorption spectra of compound **21** (*1*) and zinc 2,3,9,10,16,17,23,24-octabutylphthalocyanine (*2*) in THF.[75]

2. Mixed cyclization of phthalonitriles

Unsymmetrically substituted subphthalocyanines $\mathbf{A_2B}$ and $\mathbf{AB_2}$-types form upon random cyclization of phthalonitriles **A** and **B** in the presence of boron halides.[25, 45, 48, 68] The yields of the target non-symmetric products, for instance, of compounds **27**–**34**, rarely exceed 30% (Table 2).



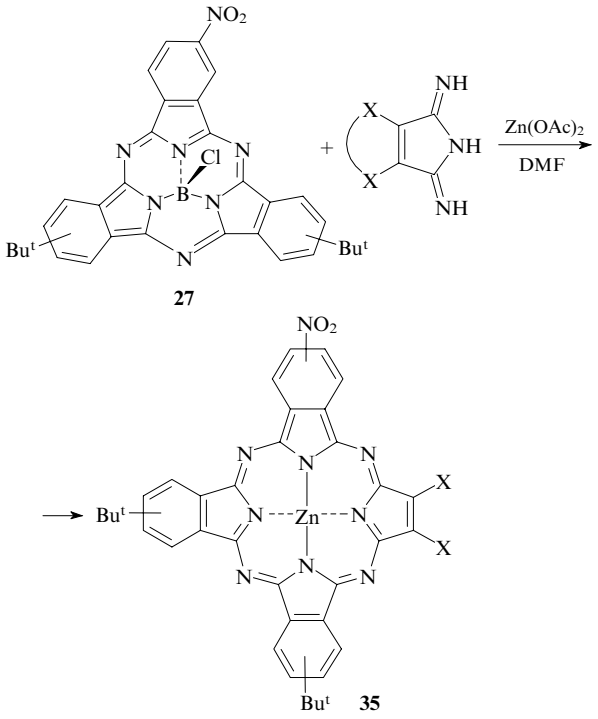
27–**34**

The composition of the products is strongly affected not only by the ratio of the starting phthalogens but also, like in the case of phthalocyanine syntheses,[77] by the reaction temperature. For example, it was reported[25] that a mixture of subphthalocyanines $\mathbf{A_2B}$ (45%), $\mathbf{AB_2}$ (45%) and $\mathbf{B_3}$ (10%) was obtained upon random cyclization of 4-*tert*-butylphthalonitrile (ring **A**) and 4-nitrophthalonitrile (ring **B**) at 220 °C. Reduction of the temperature resulted in an increase in the content of trinitrophthalocyanine $\mathbf{B_3}$. The ease of chromatographic separation of the products owing to the presence of the polar NO_2 groups was also noted.

The synthesis of unsymmetrically substituted subphthalocyanines is considered as the first step of a unique approach to the preparation of monophthalocyanines with the composition $\mathbf{A_2BC}$ (**35**), which cannot virtually be prepared by other methods.

Table 2. Yields of non-symmetrically substituted subphthalocyanines **27**–**34**.

Compound	R^1–R^4	R^5, R^6	Yield (%)	Ref.
27	$R^1 = R^4 = H$, $R^2/R^3 = Bu^t/H$	$R^5/R^6 = NO_2/H$	45	25
28	$R^1 = R^2 = R^3 = R^4 = H$	$R^5/R^6 =$ $= SC_6H_4Me\text{-}4/H$	12	45
29	$R^1 = R^2 = R^3 = R^4 = H$	$R^5 = R^6 = I$	11	48, 68
30	$R^1 = R^2 = R^3 = R^4 = F$	$R^5 = R^6 = I$	27	48
31	$R^1 = R^2 = R^3 = R^4 = F$	$R^5 = R^6 = CN$	16	49
32	$R^1 = R^2 = H$, $R^3 = R^4 = SC_8H_{17}\text{-n}$	$R^5 = R^6 = I$	21	68
33	$R^1 = R^4 = H$, $R^2/R^3 = NO_2/H$	$R^5 = R^6 = I$	6	68
34	$R^1 = R^2 = H$, $R^3 = R^4 = SO_2C_8H_{17}\text{-n}$	$R^5 = R^6 = I$	22	68



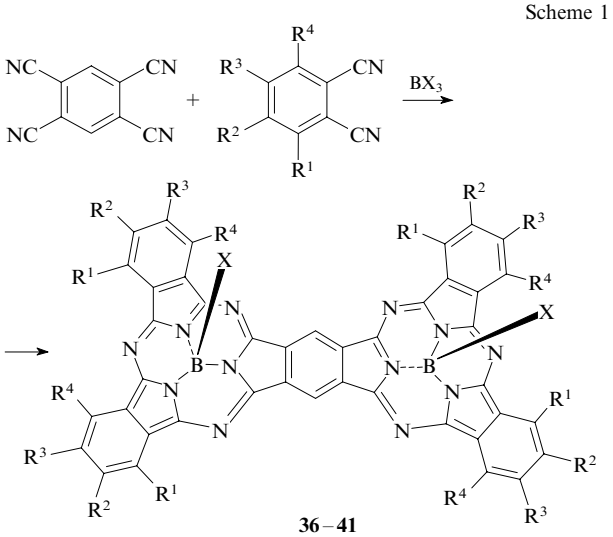
3. Bi- and polynuclear systems based on subphthalocyanines

Bi- and polynuclear planar structures possessing specific properties can be obtained from functionally substituted subphthalocyanines of the $\mathbf{A_2B}$ type.[48] Various dimers and trimers containing subphthalocyanine macrocycles linked by linear spacers (see below) can be synthesized by coupling iodosubphthalocyanines (for example, compounds **29** or **30**).

If 1,2,4,5-tetracyanobenzene is one of the components of the random cyclization of phthalonitriles in the presence of boron halides, binuclear planar subphthalocyanines **36**–**41** containing a common benzene ring are formed (Scheme 1, Table 3).[7, 24, 26, 31, 49]

For the first time, expansion of the subphthalocyanine π-system (compound **36**) was carried out in 1991 by mixed

Scheme 1



36–**41**

Table 3. Yields of binuclear subphthalocyanines **36**–**41**.

Compound	R^1–R^4	X	Yield (%)	Notes	Ref.
36	$R^1 = R^4 = H$, $R^2/R^3 = Bu^t/H$	Br	2.8		24
37	$R^1 = R^2 = R^3 = R^4 = F$	Cl	—	*syn* : *anti* = 9 : 11	7, 26, 49
38	$R^1 = R^2 = R^3 = R^4 = H$	Cl	14		49
39	$R^1 = R^4 = H$, $R^2/R^3 = I/H$	Cl	traces	low solubility	49
40	$R^1 = R^4 = H$, $R^2 = R^3 = SC_8H_{17}$-n	Cl	traces	low stability	49
41	$R^1 = R^4 = H$, $R^2 = R^3 = SC_6H_{11}$-cyclo	Cl	28		31

cyclization of 1,2,4,5-tetracyanobenzene and 4-*tert*-butylphthalonitrile.[24] Later, binuclear subphthalocyanine **37** with perfluorinated subphthalocyanine moieties has been synthesized.[7] It was found that this compound is in fact a mixture of the topoisiomers with *syn*- and *anti*-configuration, which could be separated by column chromatography (Fig. 4).

Similarity of geometric parameters of mononuclear and polynuclear subphthalocyanines[4] suggests that the subphthalocyanine molecule plays the role of an aromatic supramolecular C_3 synthon upon formation of binuclear derivatives. Hence, mononuclear subphthalocyanines may serve as building blocks in the synthesis of nano-sized aromatic heterofulleroids.[20]

Usually, unsymmetrically substituted analogues of the $\mathbf{A_2B}$ type containing peripheral CN groups (like compound **31**) or a phthalimide fragment are the side products in the preparation of binuclear planar subphthalocyanines.[49] This is in complete agreement with the authors' data[78] on the synthesis of binuclear phthalocyanines, which is in favour of similar mechanisms of formation of both phthalocyanine and subphthalocyanine macrocycles, at least, in the initial steps.

It was noted[7,49] that trinuclear analogues (compounds **42a**–**d**) are formed sometimes as admixtures along with binuclear subphthalocyanines **37**–**40**. The presence of three subphthalocyanine macrocycles results in the existence of three topoisomers with the configurations *syn*–*syn*, *syn*–*anti* and *anti*–*anti*. According to calculations, the difference in energies of topoisomers of bi- or trinuclear subphthalocyanines does not exceed 1 kcal mol^{-1}, *i.e.*, their stabilities are virtually the same. At the same time, the mononuclear analogues are more stable than the polynuclear macrocycles by *ca.* 17–20 kcal mol^{-1} according to the calculations of the relative enthalpies of formation. The stabilities of

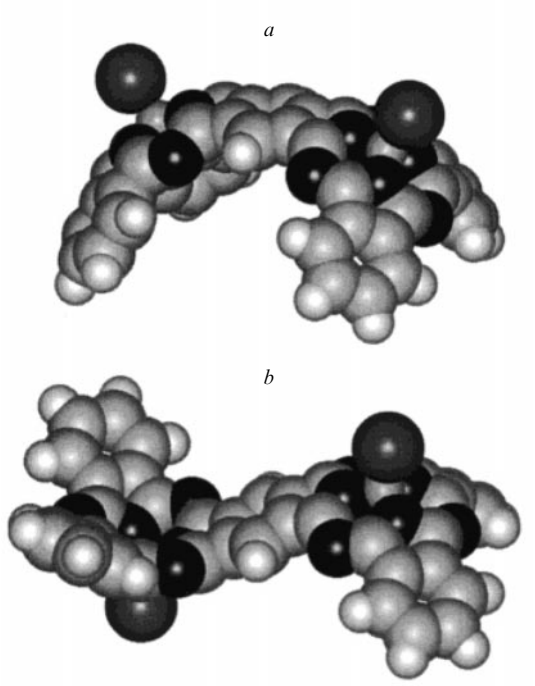
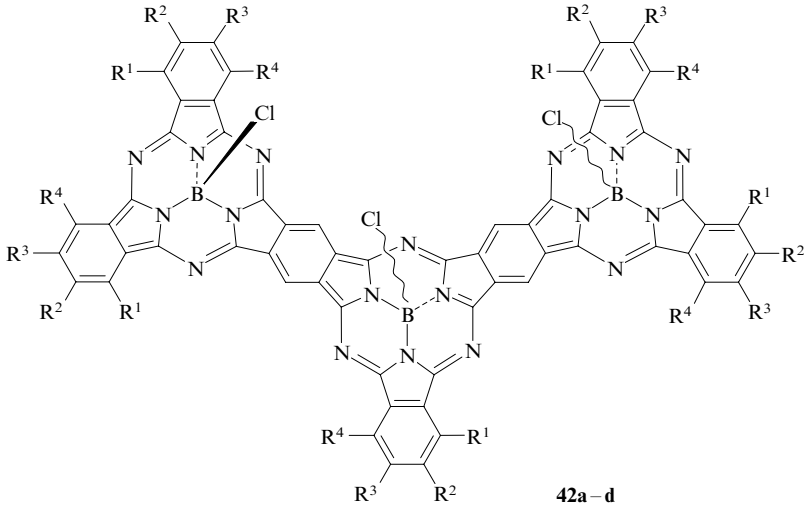


Figure 4. Structures of isomeric binuclear subphthalocyanines **37** in *syn*- (*a*) and *anti*-configurations (*b*).[7]



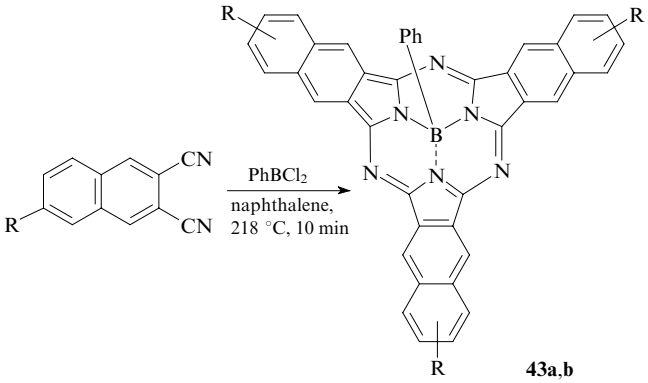
42a–**d**

$R^1 = R^2 = R^3 = R^4 =$ F (**a**), H (**b**); $R^1 = R^4 =$ H: $R^2 = R^3 =$ I (**c**), SC_8H_{17}-n (**d**).

fluoro-substituted subphthalocyanines are considerably larger than those of non-substituted analogues and those containing donor-type substituents. The difference in relative energies and symmetry of the frontier orbitals of mononuclear subphthalocyanines and bi- and trinuclear complexes suggests the extension of the π-system in the latter. This invokes bathochromic shift of the Q-band in the absorption spectra by approximately 120 and 180 nm, respectively.[49]

4. Synthesis of the subphthalocyanine analogues

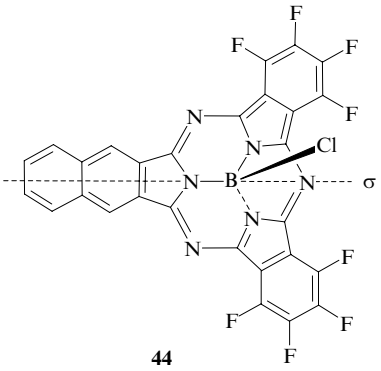
The first subphthalocyanine analogue, *viz*., subnaphthalocyanine (**43a**), was prepared by self-cyclization of 2,3-naphthalonitrile in the presence of $PhBCl_2$.[4,28] It was reported that no target products **43a**,**b** were obtained when less reactive BPh_3 was used.

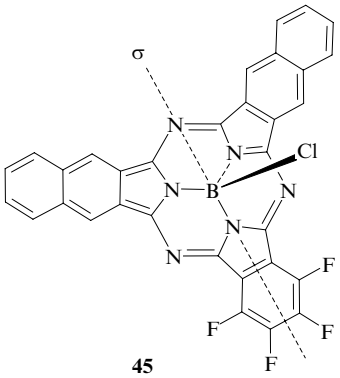


R = H (**a**), Bu^t (**b**).

Some examples of successful application of the analogous reactions of mixed boron-containing reagents have been presented above. The yields of the target subphthalocyanines **43a**,**b** did not exceed 1%; in our opinion, this is related to the low stability of these complexes against oxygen (in analogy with the corresponding naphthalocyanines). The bulky *tert*-butyl substituent in subnaphthalocyanine **43b** increases its solubility in organic solvents, which is very important from the practical point of view.

Unsymmetrically substituted subnaphthalocyanines **44** and **45** $\mathbf{AB_2}$ and $\mathbf{A_2B}$-types, respectively, were obtained for the first time by the cyclization of a mixture of 2,3-naphthalonitrile and perfluorophthalonitrile in a total yield of *ca*. 20% (σ is the symmetry plane).[6]





Both molecules possess C_s symmetry; this implies magnetic equivalence of several hydrogen atoms. This fact made it possible to discern easily the obtained isomers by ^{1}H NMR spectroscopy.[6] Additionally, the data from the X-ray diffraction of compound **44** suggest larger deviation from planarity for mixed molecules in comparison with SubPc (Fig. 5).

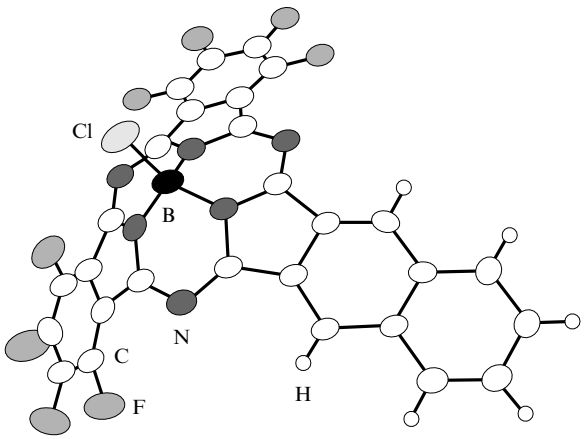


Figure 5. The structure of subphthalocyanine **44** inferred from X-ray diffraction.[6]

Unsymmetrically substituted subphthalocyanines containing naphthalene fragments possess unusual spectral characteristics. By varying the number of naphthalene fragments, one can affect the positions of the major absorption maxima in the electronic spectra. Particularly, in the case of completely fluorinated subphthalocyanine **17** the Q-band is observed at 570 nm, whereas the Q-band of compounds containing one and two naphthalene fragments (**44** and **45**) shifts to 617 and 640 nm, respectively.[6] In addition, the Q-band becomes split due to violation of symmetry (Fig. 6).

The self-cyclization of non-aromatic dinitriles in the presence of boron halides affords subazaporphyrins, unique analogues of subphthalocyanines. For the first time, compound **46a** was prepared in 1995.[4] The starting dinitrile **47** was obtained by converting commercially available 4-*tert*-butylbenzyl bromide to 4-*tert*-butylbenzyl cyanide followed by its oxidative dimerization.[79]

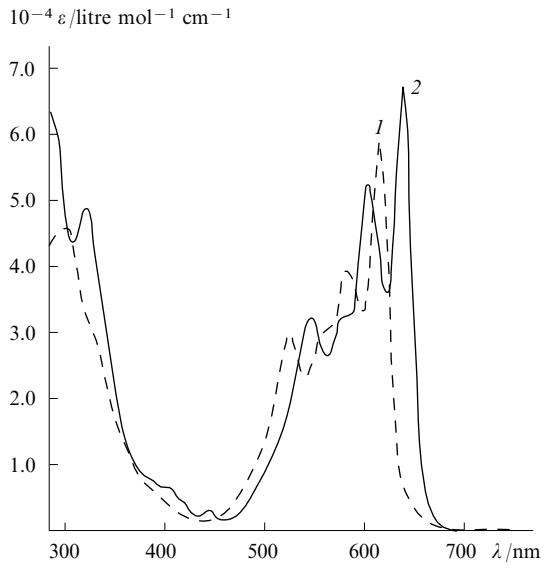
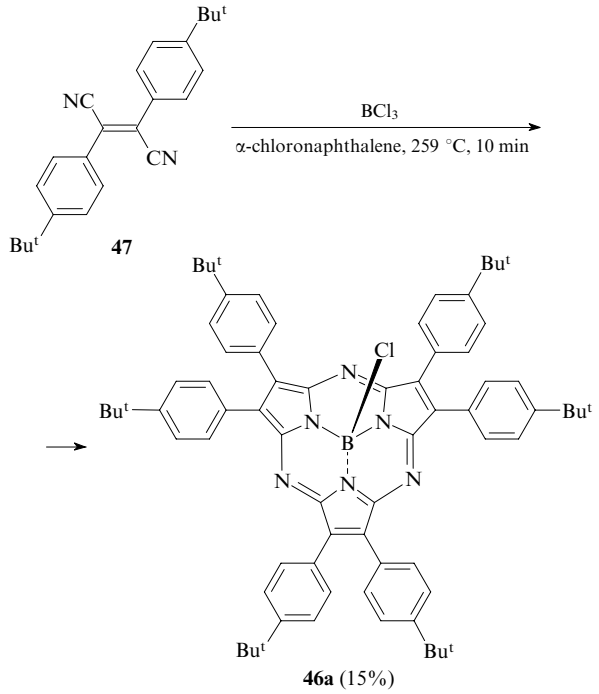
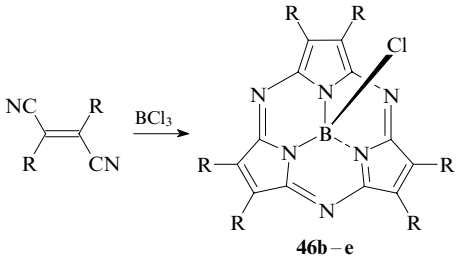


Figure 6. Electronic absorption spectra of compounds **44** (*1*) and **45** (*2*) in CH_2Cl_2.[6]



Analogous macrocyclic compounds with unique physicochemical properties are currently reported.[16, 66, 67] Subazaporphyrins intensely phosphoresce and form stable radical anions and radical cations. Like subphthalocyanines, subazaporphyrins transit from the excited singlet state [life time ($^1\tau_s$) is $\sim$3 ns] to the long-lived excited triplet state ($^3\tau_s \approx 100$ mcs), this transition is accompanied by the phosphorescence in high quantum yield (0.25). It is supposed on the basis of this observation that subazaporphyrins can be utilized as electrically active and photoactive materials in molecular photoelectric devices. In addition, distortion of the planar structure in such systems results in emergence of other unusual optical properties.

Subazaporphyrins **46b–e** were synthesized by trimerization of the corresponding substituted fumaronitriles.[66]



R = Pr^n (**b**), SC_5H_{11}-n (**c**), $SC_{12}H_{25}$-n (**d**), $SC_{18}H_{37}$-n (**e**).

Like subphthalocyanines, subazaporphyrins have 14 π-electron systems and are cone-shaped. Removal of three fused benzene rings from the subphthalocyanine backbone results in hypsochromic shift of the Q-band in the absorption spectrum by 75–80 nm.

Unusual optical properties of compounds **46c–e** (Fig. 7), *viz.*, the appearance of an intense absorption band in the lower wavelength region (n–π*-transition), have been observed.[66] It is a result of splitting of the Q-band due to the extension of π-conugation upon inclusion of electron-donating sulfur atoms. Thus, this effect is caused by the six sulfide groups attached to the pyrrole rings.

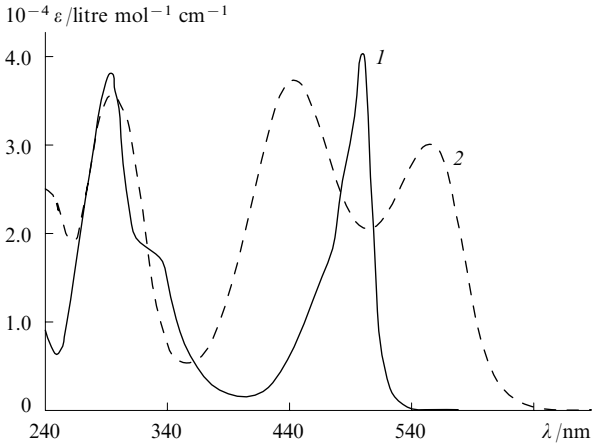


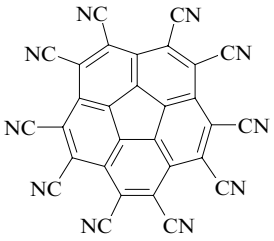
Figure 7. Electronic absorption spectra of subazaporphyrins **46b** (*1*) and **46e** (*2*) in $CHCl_3$.[66]

In contrast to subazaporphyrins **46c–e**, alkyl-substituted analogue **46b** has the electronic spectrum similar to that of subphthalocyanine **21** (see Fig. 3).

Alkylthiosubazaporphyrins **46c–e** show mesomorphism and form ordered stacks in a liquid-crystalline phase.[66, 67] The nature of the axial substituent strongly affects the supramolecular aggregation. Particularly, replacement of the chlorine atom by a hydroxyl group in compounds **46c–e** extends the temperature range in which the aggregates are stable.[66] Afterwards, subazaporphyrins containing a fluorine atom as an axial substituent could be prepared.[67] It was shown that a large dipole moment of the B–F bond results in spontaneous aggregation of the molecules in the

crystalline state with formation of ensembles of the stacking type ('stacks').

It is supposed that unusual nano-sized aromatic molecular ensemble can be formed in the reaction of decacyanocorannulene **48** with BCl_3.[20]



48

The reaction product has to include 20 subphthalocyanine macrocycles (Fig. 8). This unique heterofulleroid has not been synthesized yet.

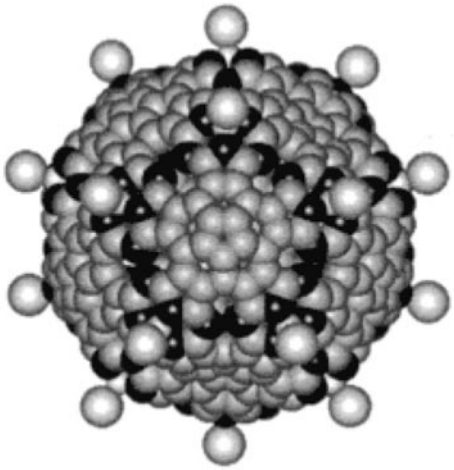


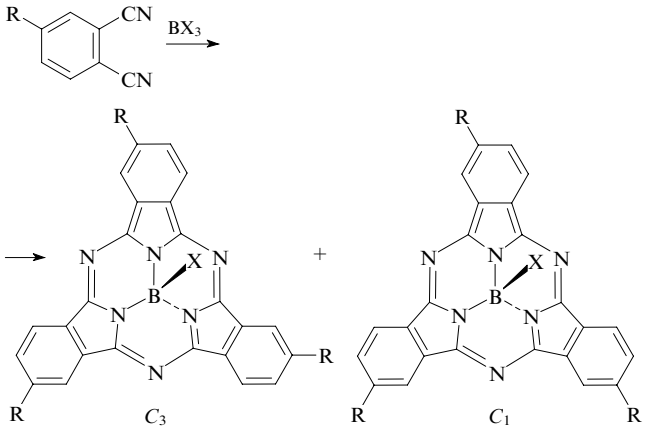
Figure 8. A hypothetical heterofulleroid formed in the cyclization of **48** with BCl_3.[20]

Thus, development of methods for the synthesis of subphthalocyanines and their analogues is a topical problem in the chemistry of macrocycles. Physicochemical studies of modified subphthalocyanines opens perspectives for the manufacture of new materials with unique properties.

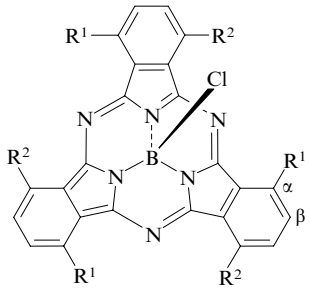
III. Stereoselectivity of formation of subphthalocyanines

If the starting phthalonitrile does not belong to the C_{2v} symmetry group, it gives a mixture of isomeric subphthalocyanines with C_1 and C_3 symmetries (compounds **1**–**15**) (see Refs 23, 44, 45, 52, 53, 58, 62).

For the first time, separation of the C_1- and C_3-isomers of subphthalocyanine **8** (R = Bu^t, X = Ph) was carried out by high-performance liquid chromatography (HPLC).[2] Later on, analogous isomers of compounds **14**, **15**, **19** were separated by preparative column chromatography on silica gel.[62] It was found that the ratio of the structural isomers is predominantly determined by the positions of peripheral substituents (α or β relative to the pyrrole ring).[34, 58]



In the case of β-substituted subphthalocyanines (compounds **1**–**15**), the ratio of isomers $C_1 : C_3$ is close to 1 : 3, *i.e.*, it corresponds to the random distribution. In the case of α-substituted subphthalocyanine **49**, this ratio is equal to ~1 : 9. This experimental fact was rationalized by Claessens and Torres[58] as being due to the steric effect of a bulky substituent located in close proximity to the macrocycle.



49

R^1/R^2 = SO_2Pr^n/H.

This explanation is based on an assumption of a hypothetical reaction of two intermediates representing a pair of azo-coupled isoindole precursors. In contrast to phthalocyanines, subphthalocyanines cannot have the centre of symmetry. Deviation from planarity deprives these molecules of the plane of symmetry coinciding with their macrocycles. As a result, the suitably substituted molecules devoid of the vertical planes of symmetry can be chiral. Each of the formed isomers represents a racemic mixture (Fig. 9). The optical isomers of compound **15** were separated by HPLC on a column with a chiral sorbent.[34]

In the case of unsymmetrically substituted subphthalocyanines, the number of possible structural and optical isomers increases. For example, the cyclization of two phthalonitriles gives a mixture of subphthalocyanines with different location of peripheral substituents (Scheme 2). The isomer ratios depend on both the steric factors and relative reactivity of phthalogens. Particularly, the cyclization of a 6 : 1 mixture of 4-nitrophthalonitrile with 4-*tert*-butylphthalonitrile results in the products of the types $\mathbf{AB}_2$, $\mathbf{A}_2\mathbf{B}$ and $\mathbf{A}_3$ in the ratio 45 : 45 : 10 (12 isomers in total).[25] At the same time, only 4 isomers form upon reaction of 2,3-naphthalonitrile with tetrafluoro-substituted or non-substituted phthalonitrile.

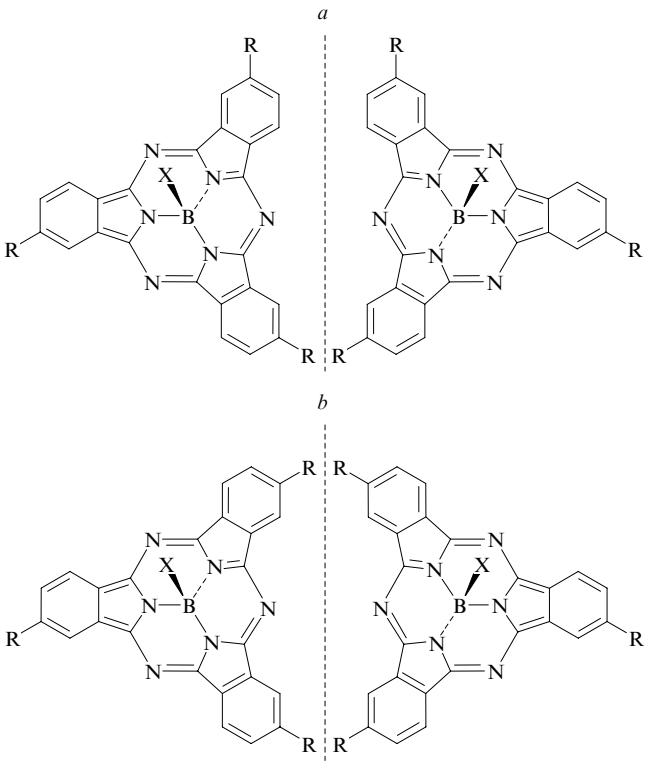


Figure 9. Schematic representation of the structural and optical isomers of subphthalocyanine obtained from unsymmetrically substituted phthalonitrile: (*a*) C_3 symmetry; (*b*) C_1 symmetry.

Thus, the selective synthesis of subphthalocyanines is a rather complicated problem. Only the use of symmetric phthalonitriles makes it possible to avoid formation of multiple isomers.

IV. Modification of the structure of subphthalocyanines and their analogues

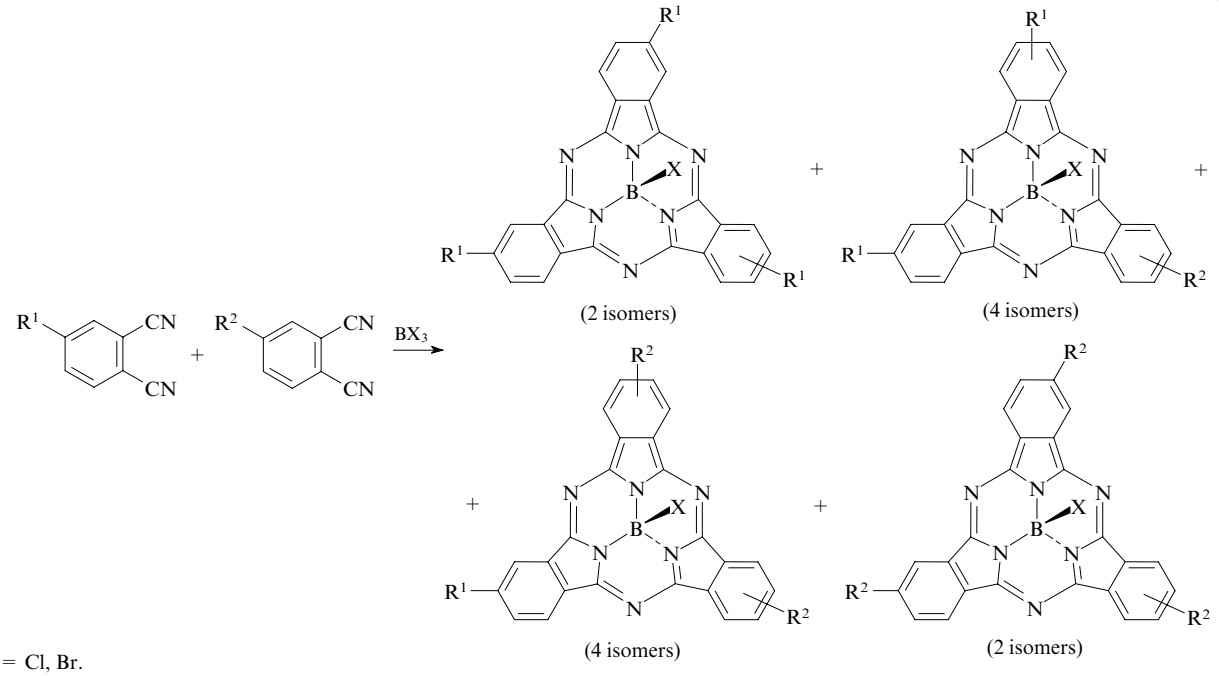
High reactivity of boron halides strongly restricts the choice of starting phthalogens and hinders prevents introduction of functional groups in the trimerization step.[20] It is the reason why the synthesis of subphthalocyanines and their analogues with required properties is carried out in at least two steps: cyclization is followed by modification of the structure. There are three major types of modification, *viz*., the substitution of the axial halogen atom,[3, 7, 9–11, 15, 17–19, 46, 47, 49–51, 56, 57, 59, 62] reactions involving peripheral substituents[18, 45, 48, 50, 64, 68] and expansion of the subphthalocyanine macrocycle.[2, 20, 77] The first two types retain the number of π-electrons in the macrocyclic system, whereas the ring expansion results in both the changes in the conjugation system and increase in the symmetry of a molecule.

1. Nucleophilic substitution of the axial halide atom

The high mobility of the axial halogen atom considerably hampers isolation and chromatographic purification of the target products. For instance, side products with the OH group in the axial position formed in syntheses of bromo-substituted compounds **1**–**6**.[23, 53] Similar substitution proceeds to a lesser extent in the case of subphthalocyanines **7**–**21** with the axial chlorine atom because of the greater polarity of the B—Cl bond. It was shown that peripheral substituents significantly affect the stability of the products against undesirable nucleophilic substitution in the course of chromatographic purification. Electron-withdrawing substituents (F, NO_2) prevent hydrolysis of subphthalocyanines, while electron-donating substituents (Alk, SAlk) favour this reaction.[2, 25]

Macrocycle **50** was synthesized for the first time by hydrolysis of non-substituted subphthalocyanine **16** with the axial chlorine atom (Scheme 3).[2] The nucleophilic sub-

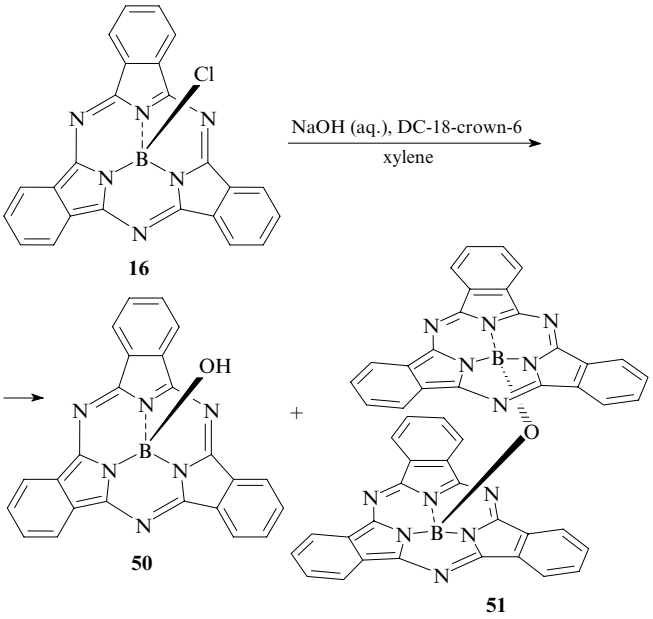
Scheme 2



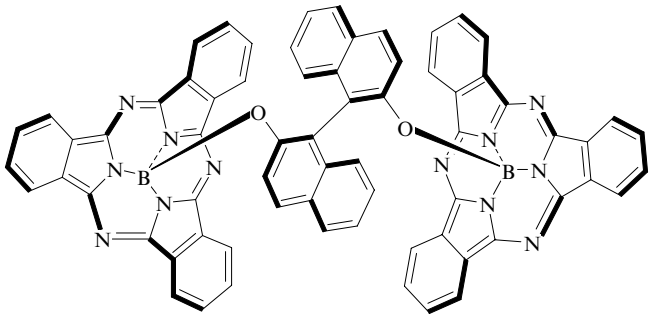
X = Cl, Br.

stitution was carried out in an alkaline medium in the presence of a phase-transfer catalyst, dicyclohexyl-18-crown-6 (DC-18-crown-6). Along with the target product **50**, μ-oxo complex **51** was detected (analogous complexes are known for iron phthalocyanine [80]). It turned out that the content of compound **51** in the reaction mixture increases upon prolonged contact of the starting subphthalocyanine with NaOH, therefore the conclusion was made that complex **50** is an intermediate. Broadening and hypsochromic shift of the Q-band in the spectra of subphthalocyanine μ-oxo complexes [2] are analogous to those of binuclear phthalocyanines of the clamshell type.[81]

Scheme 3



The interest in dimeric subphthalocyanines has recently greatly increased. Thus structurally similar compounds **52** (Ref. 11) and **53** (Ref. 3) were described. Subphthalocyanine moieties in complex **52** are linked by the B—B bond (Fig. 10), while 1,1′-binaphthyl-2,2′-diolate (BINOL) dianion is a spacer in macrocycle **53**.



Subphthalocyanines similar to compound **50** are often used as precursors of silicon-containing derivatives (like compound **54**), which cannot be synthesized by other means.[2]

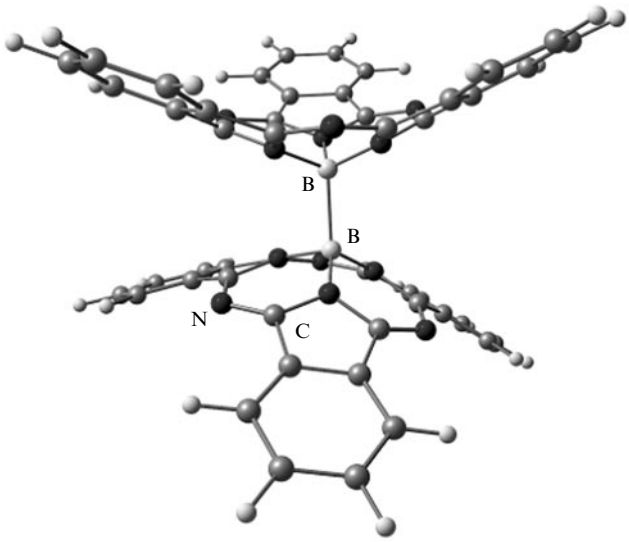
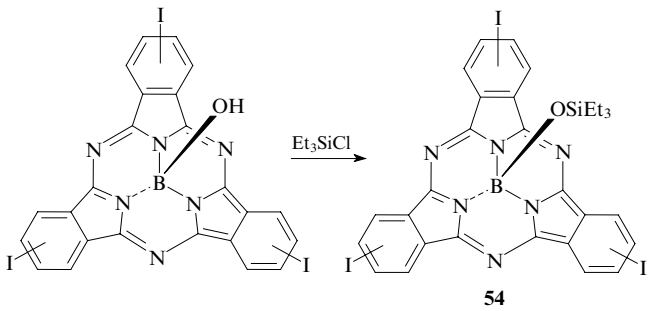
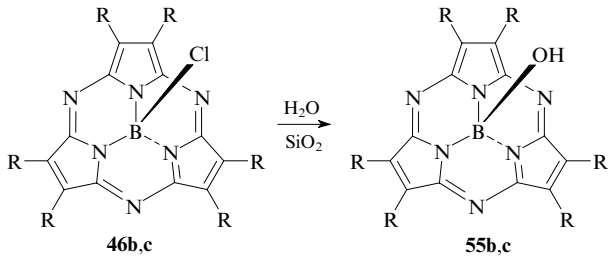


Figure 10. DFT-optimized structure of subphthalocyanine complex **52**.[11]



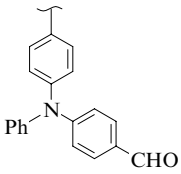
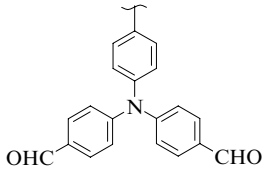
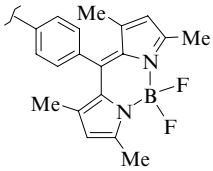
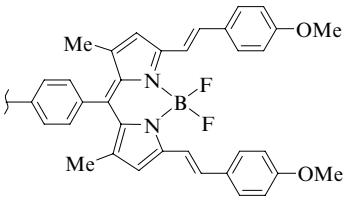
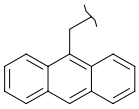
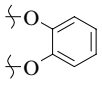
Hydrolysis of the axial chlorine atom yielding the hydroxyl analogues was successfully carried out by example of subazaporphyrins **46b**,**c**.[16, 66] This reaction occurs under the action of SiO_2 in the presence of water; however, the yields of compounds **55b**,**c** did not exceed 10%. This was explained by the lesser stability of the subazaporphyrin macrocycle in comparison with the subphthalocyanine one.



R = Pr^n (**b**), SC_5H_{11}-n (**c**).

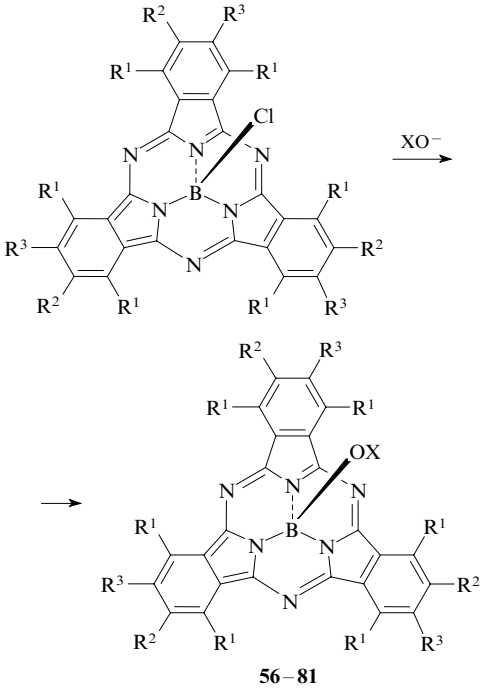
Aliphatic alcohols and phenols are conventional nucleophiles in the syntheses of axial derivatives of subphthalocyanines and their analogues.[9, 46, 50, 51, 56, 59] Various subphthalocyanine derivatives **56**–**81** (Table 4) have been

Table 4. Yields of subphthalocyanines **56**–**81**.

Compound	R^1–R^3	X	Yield (%)	Ref.
56	$R^1 = R^2 = R^3 = H$	H	82	51
57	$R^1 = R^2 = R^3 = H$		64	46
58	$R^1 = R^2 = R^3 = H$		94	46
59	$R^1 = R^2 = R^3 = H$		90	9
60	$R^1 = R^2 = R^3 = H$		90	9
61	$R^1 = R^2 = R^3 = H$	$CH_2CH_2NMe_2$	35	17
62	$R^1 = R^2 = R^3 = H$	$C_6H_4CO_2H$-4	27	17
63	$R^1 = R^2 = R^3 = H$	Py-3(4)	see [a]	17
64	$R^1 = R^2 = R^3 = H$		25	19
65	$R^1 = R^2 = R^3 = H$	Bn	79	19
66	$R^1 = R^2 = R^3 = H$	Ph	84	19
67	$R^1 = R^2 = R^3 = H$	$CH_2C_6H_3Me_2$-3,5	83	19
68	$R^1 = R^2 = R^3 = H$	$C_6H_3Me_2$-3,5	79	19
69	$R^1 = R^2 = R^3 = H$	$CH_2C_6H_4Me$-4	84	19
70	$R^1 = R^2 = R^3 = H$	C_6H_4Me-4	79	19
71	$R^1 = R^2 = R^3 = F$	$C_6H_4(C_6H_4NPh_2$-4)-4	45	56
72	$R^1 = R^2 = R^3 = F$	$C_6H_4CO_2H$-4	56	59
73	$R^1 = R^2 = R^3 = F$	C_6H_4CHO-3	76	62
74	$R^1 = R^2 = R^3 = F$	Ph	34	7
75	$R^1 = H$, $R^2/R^3 = I/H$	Ph	24 [b]	50
76	$R^1 = H$, $R^2/R^3 = I/H$	$C_6H_3Bu^t_2$-3,5	12	10
77	$R^1 = H$, $R^2/R^3 = OPy$-3/H	3-Py	63	50
78	$R^1 = H$, $R^2/R^3 = OPy$-3/H	Ph	80	50
79	$R^1 = H$, $R^2/R^3 = NO_2/H$	Ph	58	51
80	$R^1 = H$, $R^2/R^3 = OPh/H$	Ph	80	51
81	$R^1 = H$, R^2–R^3 = 	C_6H_4CHO-2	39	10

[a] Yield of the isomer substituted in position 3 is 54%, yield of the isomer substituted in position 4 is 24%; [b] the total yield with account of the step of formation of subphthalocyanine.

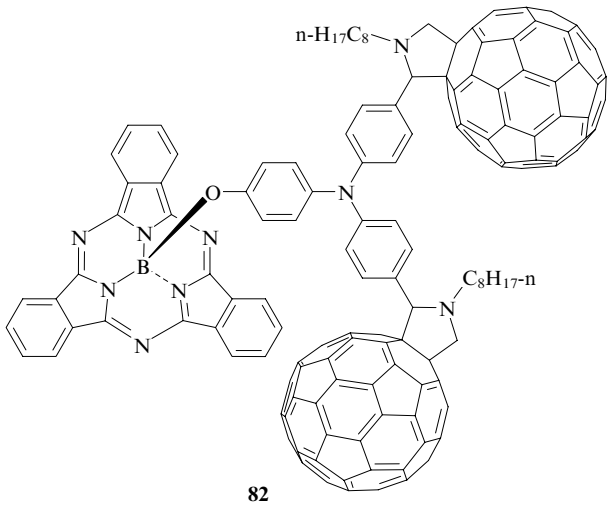
obtained to date. This makes it possible to consider subphthalocyanine macrocycle as a suitable building block for the preparation of nano-sized molecules.



56–81

The presence of aldehyde groups in the axial substituents of compounds **57**, **58**, **73** and **81** made it possible to prepare hybrid structures like compound **82** with subphthalocyanine and fullerene fragments.[10, 18, 46]

Similar fullerene derivatives are also known for binuclear subphthalocyanines containing a common benzene ring.[47, 57]



82

Subphthalocyanine molecules containing fullerene or boron–dipyrrole fragments (like compound **59**, **60**) are convenient models for studies of energy transfer processes.[9, 10]

Heteronuclear complexes of subphthalocyanines with other macrocyclic compounds are of special interest. For instance, we synthesized complexes **83a**,**b** including subphthalocyanine and phthalocyanine macrocycles by the reaction of compound **26** with functionally substituted phthalocyanines (Fig. 11).[75]

Because of specific orientation of the macrocycles in these complexes, the usual aggregation process is violated so that compounds **83a**,**b** are well soluble in organic solvents (from petroleum ether to alcohols, DMF, DMSO). Combination of different macrocycles in one molecule determines unusual physicochemical properties of complexes **83a**,**b**, which are currently being intensively studied.

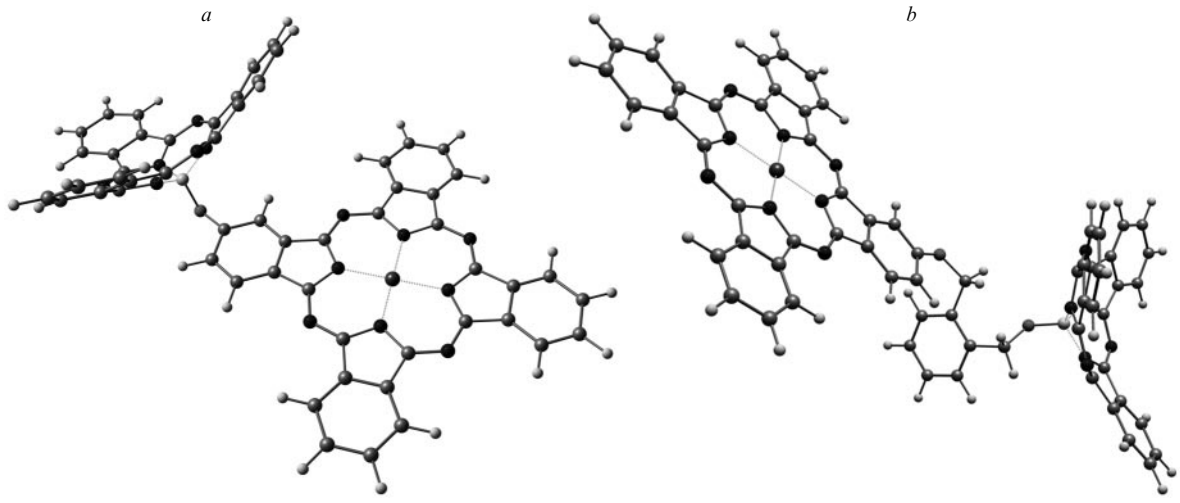
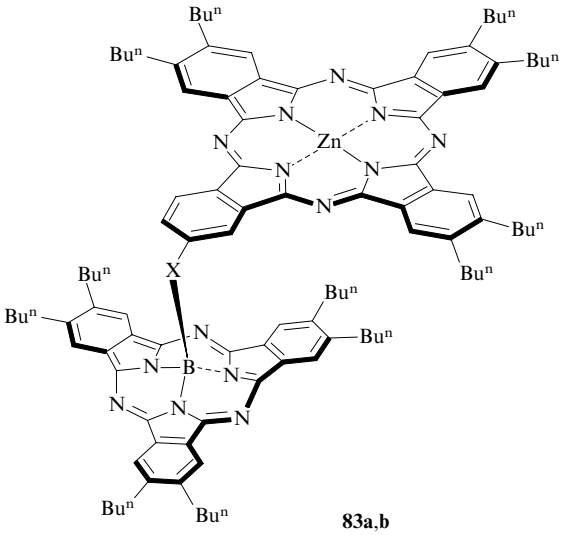
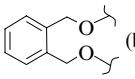


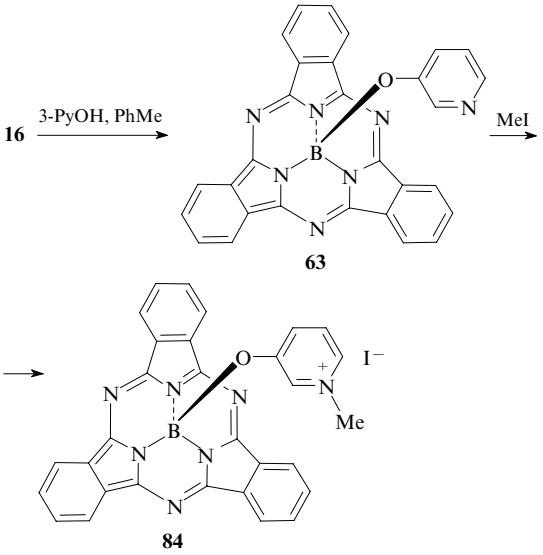
Figure 11. Optimized (DFT//PBE/3z) structures of heteronuclear complexes of types **83a** (*a*) and **83b** (*b*) (for simplicity, the calculations were performed for non-substituted compounds).



83a,**b**

X = O (**a**),  (**b**).

In some cases, the introduction of certain axial substituents enables solubility of subphthalocyanines in water (for example, water-soluble iodomethylate **84** is formed upon quaternization of compound **63**).[17, 50]



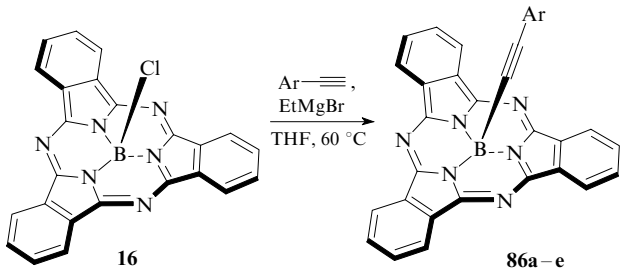
Hydrophilicity of subphthalocyanines is required for further studies of these compounds as photosensitizers with the aim of their application in photodynamic therapy of cancer.

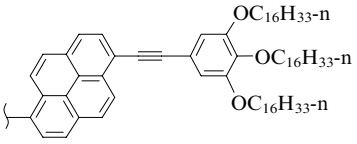
Incorporation of a pyridine fragment into the axial substituent makes it possible to obtain supramolecular structures based on these subphthalocyanines. For instance, the formation of the coordination bond between the pyridine nitrogen atom in compound **63** and the metal ion from the porphyrin complex results in compound **85** (Scheme 4).[8]

When speaking of the intermolecular coordination, it is necessary to mention the study by Claessens and Torres[7] where a specific packing of molecules of subphthalocyanine **74** due to hydrogen bonding H···F (Fig. 12) in the crystalline state was demonstrated for the first time by X-ray diffraction.

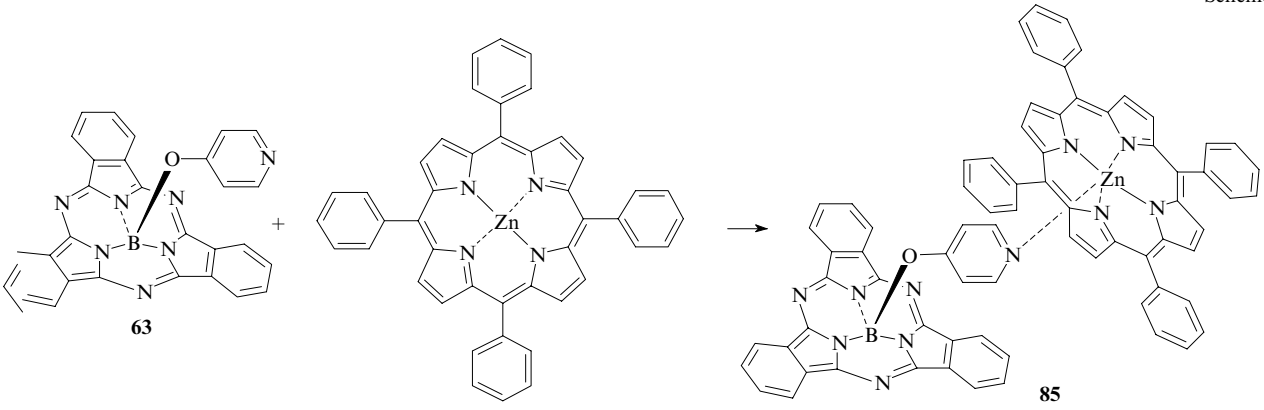
As has been mentioned above, substitution of the axial halogen atom in reactions with alcohols or alcoholates is a most popular method for the modification of the subphthalocyanine structure. However, there are examples of an analogous nucleophilic substitution reaction with other nucleophiles, *e.g.*, salts of carboxylic acids and some C-nucleophiles.[2, 69]

When an excess of phenyllithium was employed in an analogous reaction to prepare subphthalocyanine **23**, decomposition of the macrocycle occurred.[2] It was supposed that the decomposition products are 'opened' subphthalocyanine. Later, this supposition was confirmed experimentally and formed the basis for the development of a new method for the synthesis of unsymmetrically substituted monophthalocyanines with the composition $\mathbf{A_3B}$ (see Section IV.3). At the same time, reactions with stoichiometric amounts of the Grignard reagents afford the target products **86a**–**e** in 22%–74% yields.[15]



Ar = $R_nC_6H_{5-n}$ [R_n = 4-Me (**a**), 4-I (**b**), 3,4,5-(n-$C_{16}H_{33}O)_3$ (**c**), 4-Bu^n_2N (**d**)];  (**e**).

Scheme 4



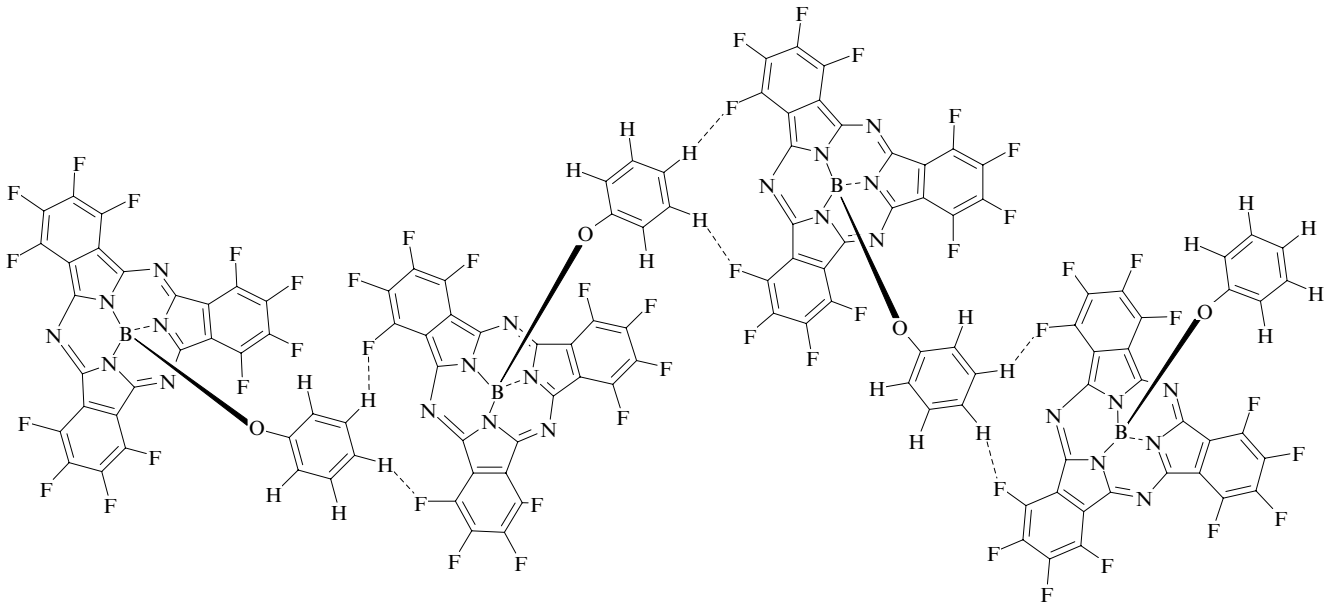


Figure 12. Schematic representation of hydrogen bonds in crystals of molecules **74**.[7]

Physicochemical studies of ethynyl-substituted subphthalocyanines **86c**,**e** containing pyrogallol ether fragments conjugated with the macrocycles demonstrated that these compounds are promising fluorophores.

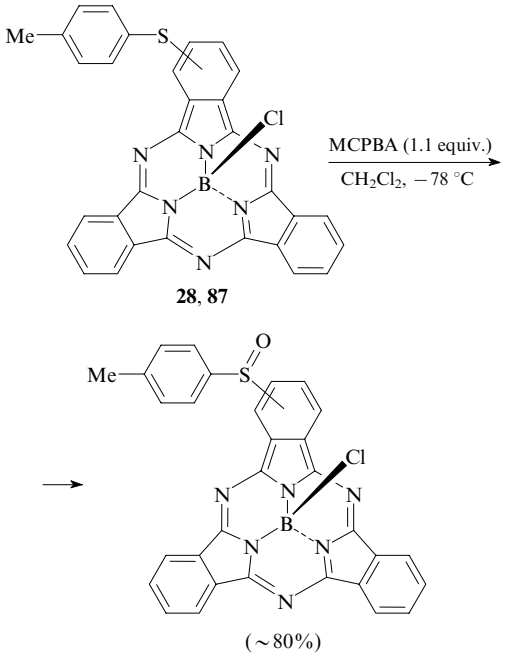
Interestingly, the presence of a donor group (compound **86d**) significantly increases the fluorescence quantum yield, while protonation of the Bu^n_2N fragment (by titration with $HClO_4$) prevents electron transfer from the aryl group to the subphthalocyanine macrocycle. No decomposition of the compound occurs upon repeated protonation–deprotonation and this process can be carried out cyclically. We suppose that the axial modification of subphthalocyanines with alkynyl C-nucleophiles is a promising way to new materials for photoelectronics.

Thus, owing to high mobility of the axial halogen atom, it is possible to prepare various supramolecular structures including conjugates of the type 'subphthalocyanine–fullerene' and heteroligand complexes with unique properties.[75]

2. Modification of the periphery of the macrocycle

Reactions of subphthalocyanine involving only peripheral substituents in the benzene rings that do not affect the backbone and the axial substituent are documented. The reactions of this kind are known for both non-symmetric and symmetric subphthalocyanines.

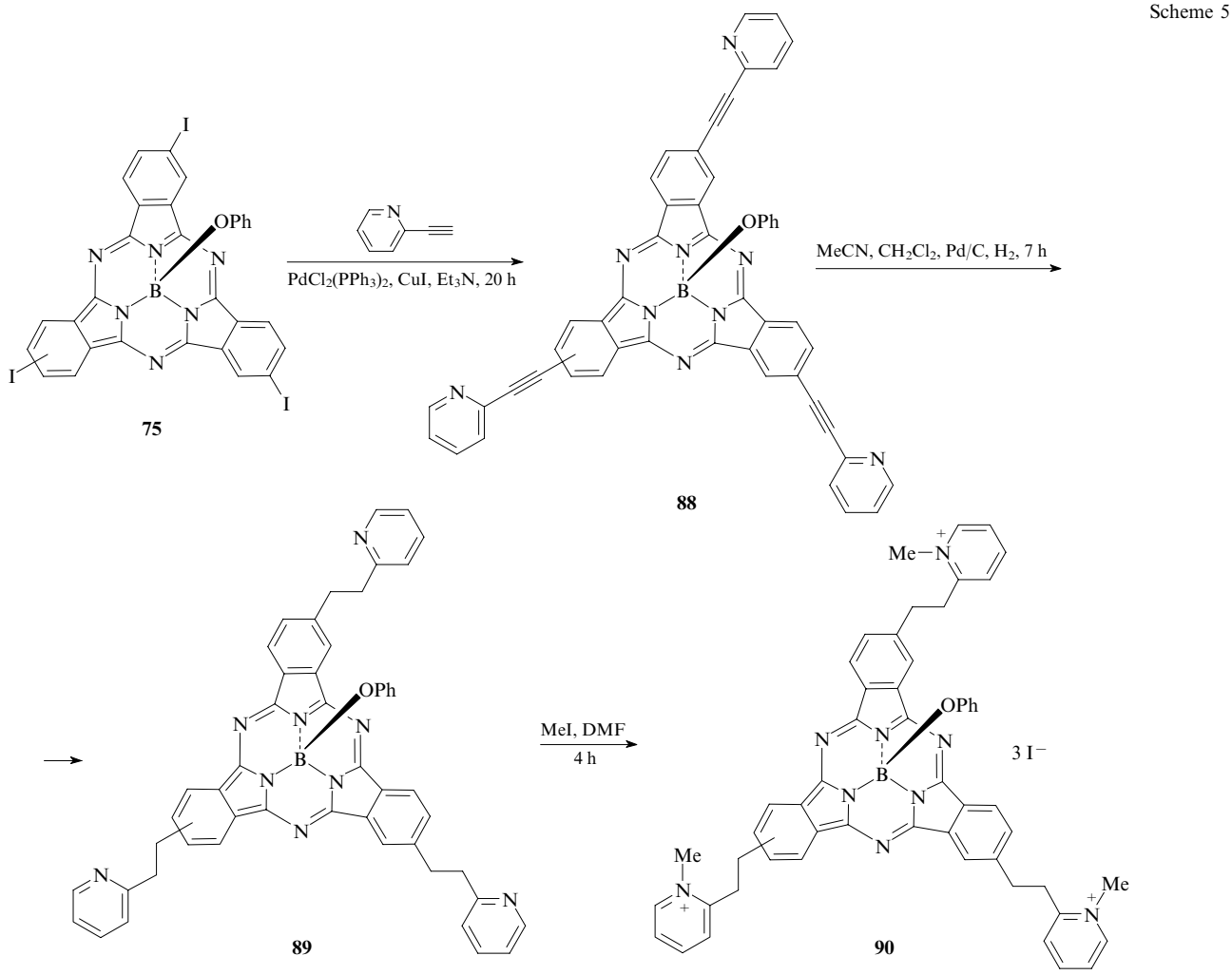
In some cases, the position of the substituent in the molecule influences the process selectivity. An example of this influence is the oxidation of unsymmetrically substituted subphthalocyanines **28** and **87**, which were obtained by the cyclization of a nine-fold excess of non-substituted phthalonitrile with 3- and 4-(*p*-tolylthio)phthalonitriles, respectively, in the presence of BCl_3, with *m*-chloroperbenzoic acid (MCPBA). Oxidation of subphthalocyanine **87** containing the 4-MeC_6H_4S group in the α-position affords a 95 : 5 mixture of diastereoisomers according to the ^1H NMR data. In contrast, compound **28** containing this substituent in the β-position gives equimolar mixture of the diastereoisomers in the analogous reaction.[45]



Isomers: α (**87**), β (**28**).

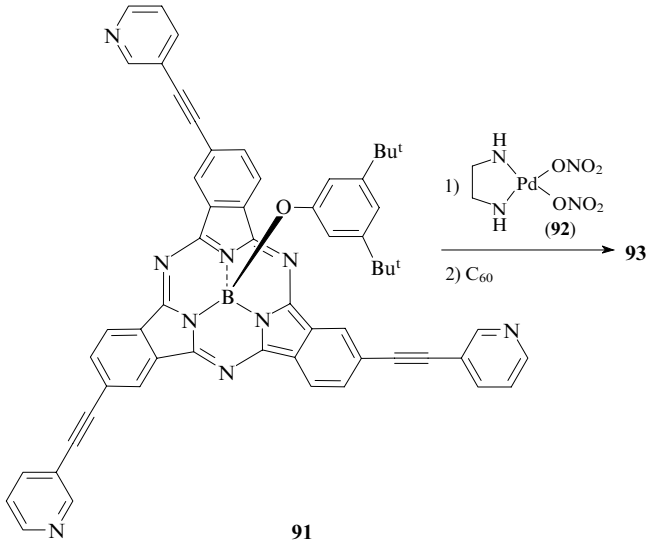
Subphthalocyanines can be modified by the cross-coupling reactions of macrocycles bearing definite peripheral substituents with alkynyl reagents. Some functional groups required to impart special properties to the target products can be introduced into the subphthalocyanine structure in this way.[10, 18, 45, 48, 50, 64, 68] However, it is worth noting that the range of suitable starting phthalocyanines is extremely limited as the appropriate compound has to contain iodine atoms. Such subphthalocyanines are synthesized by either the cyclization of 4-iodo- (see Ref. 50) or 4,5-diiodophthalonitriles[48] or co-cyclization of these phthalogens with other substituted phthalonitriles. Thus a strategy was developed[50] (Scheme 5) for the preparation of substituted subphthalocyanines, including water-soluble ones.

Scheme 5



The cross-coupling of triiodosubphthalocyanine with 3-ethynylpyridine in the presence of a palladium catalyst gives the target product **88** in 42% yield. Catalytic hydrogenation of the triple bonds followed by quaternization of **89** with methyl iodide results in water-soluble subphthalocyanine **90**. Quaternization of subphthalocyanine **89** brings about significant changes in electronic absorption spectra consisting of a decrease in the Q-band intensity and its broadening. This conforms to our studies of intramolecular interactions in binuclear bridged phthalocyanines;[77] however, in the present case this is due to the formation of molecular stacks caused by a strongly polar media, *viz*., by water. It is noteworthy that the subphthalocyanine macrocycle, less stable in comparison to phthalocyanine, is not virtually destroyed under the conditions of the cross-coupling reaction. The impetus to the development of the complex approach described above was the fact that subphthalocyanine **89** cannot be obtained from 4-[2-(3-pyridyl)ethyl]phthalonitrile.[50]

Analogues of compound **88** are also interesting for the preparation of nano-sized molecules.[10] Particularly, upon interaction of subphthalocyanine **91** with palladium complex **92**, the cage-like macromolecule is formed, which can enclose a molecule of fullerene C_{60}.



Such a supramolecular capsule can selectively extract a molecule of fullerene C_{60} from the solid phase and stabilize it between two bulged surfaces of the subphthalocyanine macrocycles by formation of **93** (Fig. 13). In essence, this is a new method for the isolation of the valuable product.

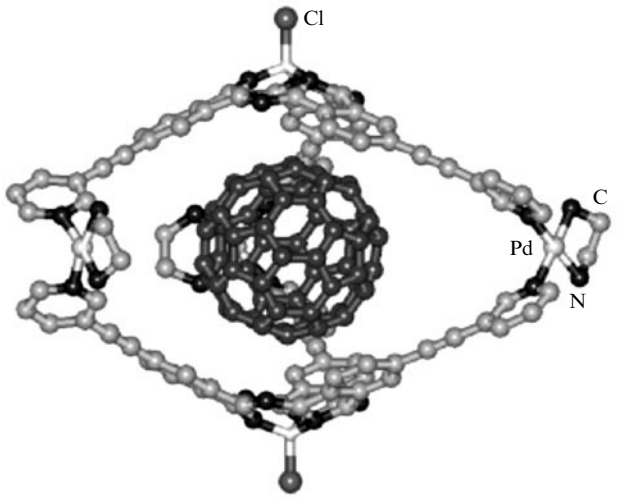


Figure 13. The structure of macromolecule **93** with enclosed fullerene C_{60} (the calculation is performed for unsubstituted analogue possessing the axial Cl atom).[10]

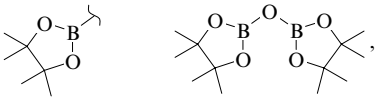
Decapsulation of fullerene is effected by treatment of supramolecule **93** with NH_4PF_6.[55]

The presence of two *ortho*-iodine atoms in one of the isoindole fragments of subphthalocyanines makes it possible to synthesize bi- and polynuclear macrocycles (Scheme 6).[48] For instance, substituted phthalocyanines **94a**,**b** were obtained in two steps from compounds **29** and **30** in total yields of *ca.* 30%. It was noted[48] that conventional conditions are not suitable for their coupling to dehydroannulene trimers **95a**,**b** since strong bases cause opening of the subphthalocyanine macrocycle. Therefore, the preference was given to the mild conditions of trimerization in the presence of a palladium catalyst and a weak nucleophile, 1,4-diazabicyclo[2.2.2]octane (DABCO). The target rimers **95a**,**b** were obtained in ~20% yields. As in the case of analogous phthalocyanine derivatives,[82] the formation of dimers with a common tetrayne ring was expected, along with compounds **95a**,**b**; however, only subphthalocyanines **96a**,**b** were detected in trace amounts. It is supposed that compounds **95a**,**b** are formed as mixtures of topoisomers; however, it could not be proved experimentally. According to the ^{1}H NMR spectroscopy data, the only 'closed' conformation is typical of these compounds, whereas dimers **96a**,**b** exist in the 'opened' form. Due to extension of the conjugation system, the absorption maxima in the electronic spectra of subphthalocyanines **95a**,**b** are bathochromically shifted by ~40 nm relative to those of the starting compounds **29** and **30**. In addition, compounds **95a**,**b** are characterized by higher electroactivity in comparison with their mononuclear analogues, although this is a rather special research topic.

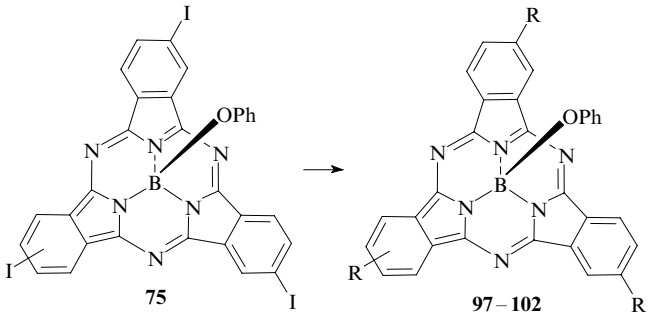
Several other coupling reactions involving peripheral iodine atoms were reported.[64] They result in high-yielding transformations of compound **75** to subphthalocyanines **97**–**102** containing various functional groups (Table 5). All these reactions (the Stille and Suzuki reactions, amination and borylation reactions) are catalyzed by palladium complexes.

The synthesis of compounds **97**–**102** is an example of preparation of different nano-sized structures and supramolecular ensembles. It is necessary to emphasize that the cross-coupling reactions considered in this section make it possible to modify the structure of the subphthalocyanine macrocycle without its decomposition. Some reduction in yields of the target products is caused by partial ring-opening under the action of bases or basic reagents used in these reactions.

Table 5. Modification products of subphthalocyanine **75** by reactions involving the peripheral iodine atoms.

Compound	R	Conditions and reagents	Yield (%)
97	$CH{=}CH_2$	$Bu^n_3SnCH{=}CH_2$, $Pd(PPh_3)_4$, PhMe, Δ	72
98	$C{\equiv}CH$	$Bu^n_3S{\equiv}CH$, $Pd(PPh_3)_4$, PhMe, Δ	64
99	Ph	$PhB(OH)_2$, $Pd(PPh_3)_4$, CsF, DME, Δ	87
100	NPh_2	Ph_2NH, $Pd_2(dba)_3$, BINAP, Cs_2CO_3, PhMe, Δ	87
101	$N(CH_2)_5$	$(CH_2)_5NH$, $Pd_2(dba)_3$, BINAP, Cs_2CO_3, PhMe, Δ	74
102		$PdCl_2(dppf)$, KOAc, DMSO, 70 °C	62

Notes. DME is 1,2-dimethoxyethane, dba is dibenzylideneacetone, BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, dppf is 1,1-bis(diphenylphosphino)ferrocene.

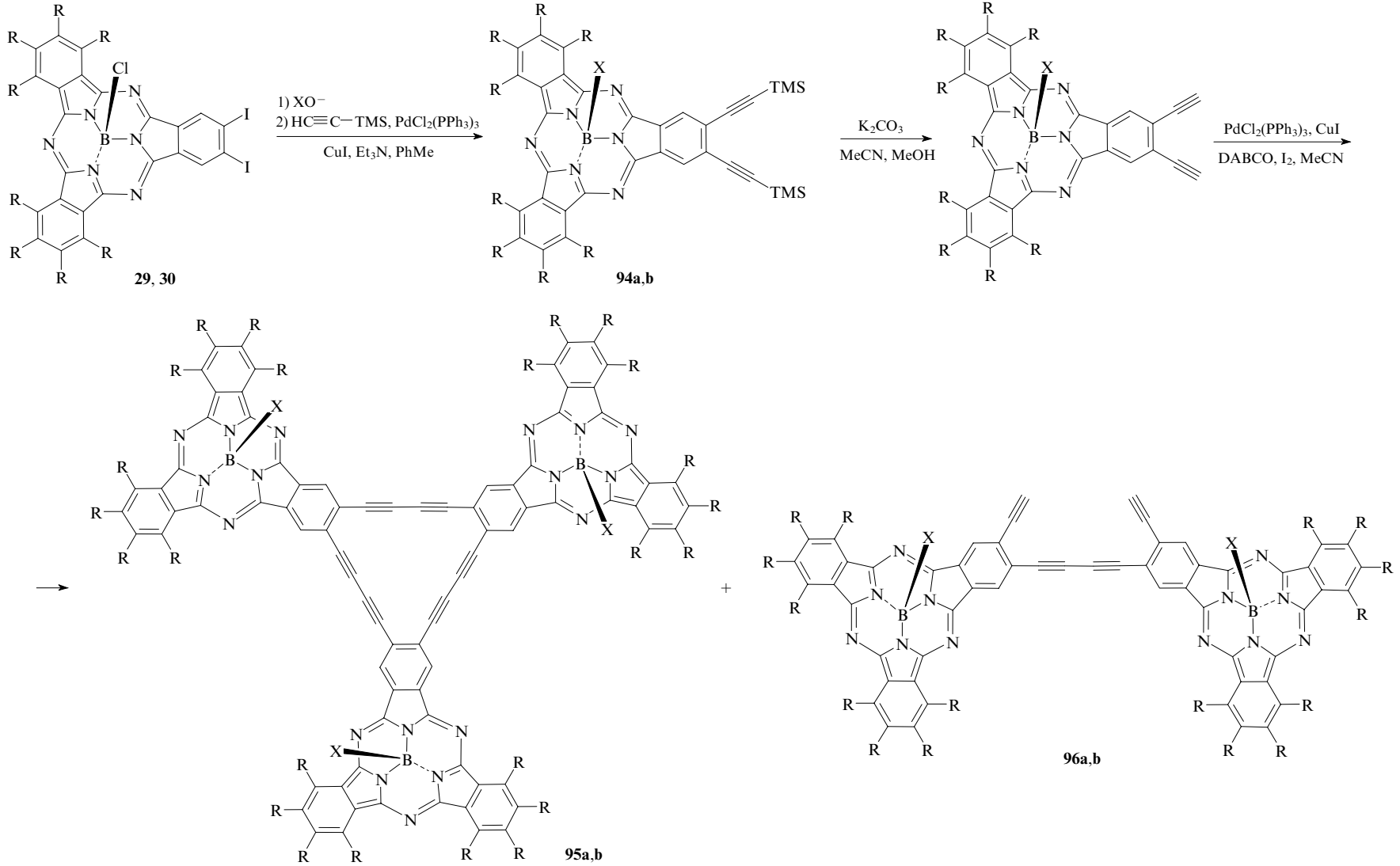


3. Expansion of the subphthalocyanine macrocycle

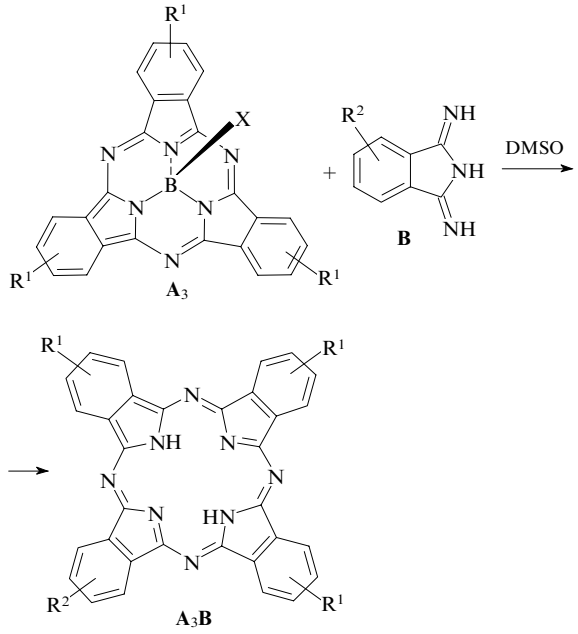
The nucleophilic substitution and cross-coupling reactions involving peripheral groups in subphthalocyanines have been discussed above. As has already been mentioned, these processes do not result in the change in the number of π-electrons in the macrocyclic system. However, owing to partial decrease in aromaticity because of deviation from planarity in subphthalocyanines, it becomes possible to carry out reactions resulting in expansion of the macrocycle.[2] In our previous review,[77] we mentioned such transformations resulting in the synthesis of unsymmetrically substituted monophthalocyanines with the composition $\mathbf{A_3B}$.

The general scheme of expansion of the subphthalocyanine macrocycle is as follows:[2]

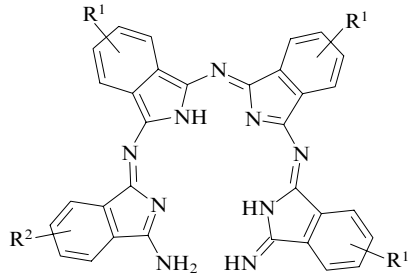
Scheme 6



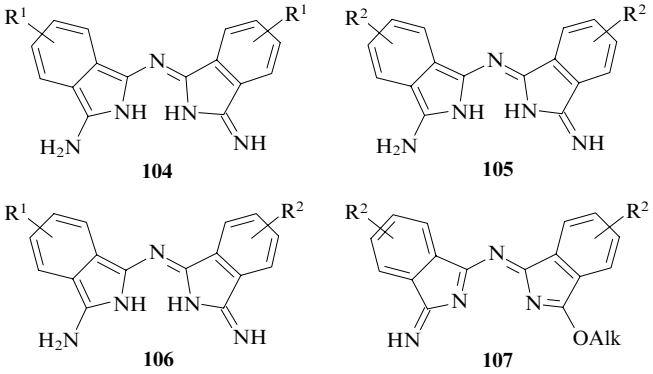
For compounds **94**–**96**: R = H, X = Ph (**a**); R = F, X = $C_6H_3Bu^t_2$-3,5 (**b**); TMS is trimethylsilyl.

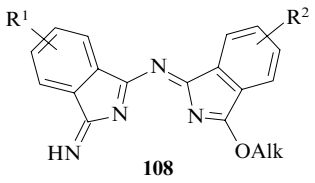


The nature of the 1,3-diiminoisoindoline component **B** has special effect on the selectivity of the process and yield of the target phthalocyanines. Donor substituents in the reagent **B** and acceptor substituents in subphthalocyanine $\mathbf{A}_3$ increase the yield of phthalocyanine $\mathbf{A}_3\mathbf{B}$. In the course of the reaction, thermal opening of the subphthalocyanine macrocycle takes place, which is followed by the subsequent reaction of the intermediate trimer with the component **B**. This sequence of transformations results in 'opened' phthalocyanine **103**,[44,83] which then undergoes closure.

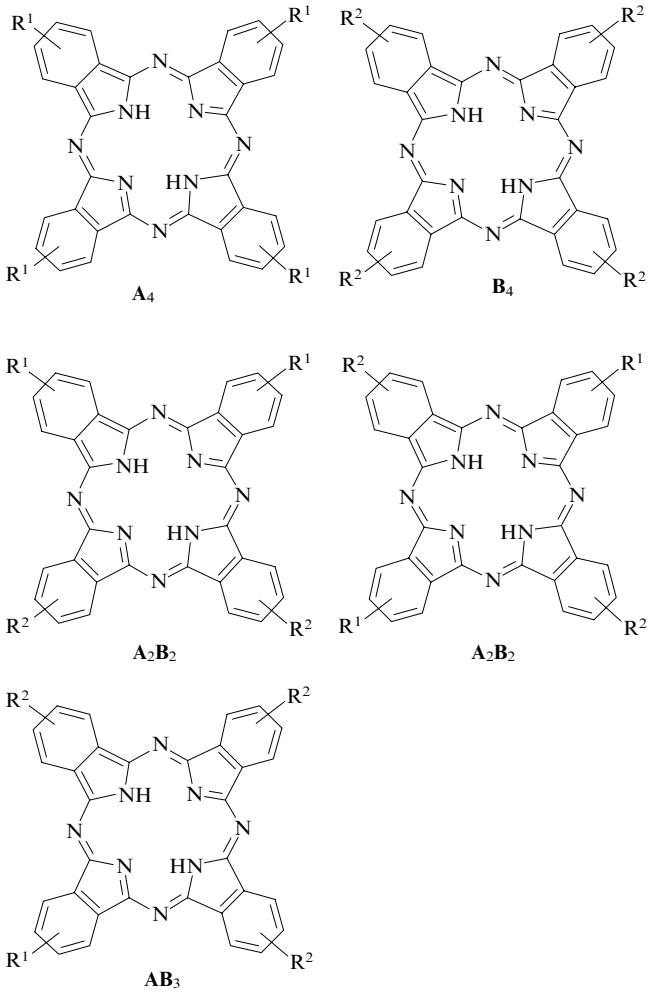


However, alternative pathways of the process cannot be excluded, such as fragmentation to intermediates **104**–**106**, and also, in the presence of alcoholates, to ethers **107**, **108**.





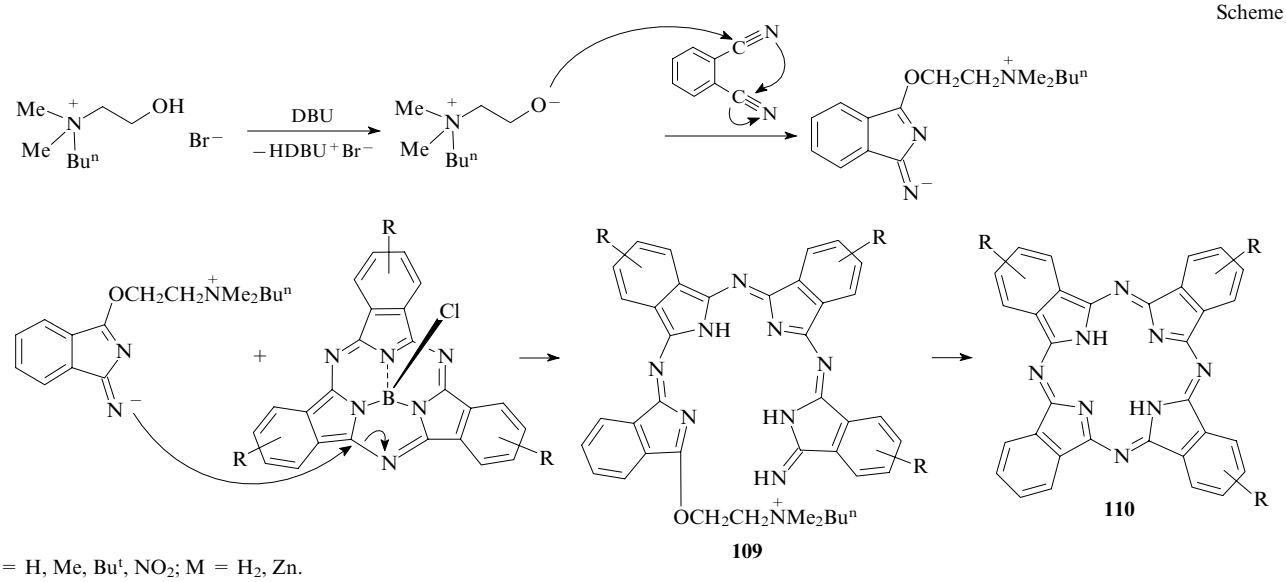
As a result, other symmetric ($\mathbf{A}_4$, $\mathbf{B}_4$) and non-symmetric ($\mathbf{AB}_3$, $\mathbf{A}_2\mathbf{B}_2$) phthalocyanines form along with the compound $\mathbf{A}_3\mathbf{B}$, which is often observed experimentally.



In 2009, Chauhan and Kumari[44] succeeded in the optimization of the conditions of the expansion of the subphthalocyanine macrocycle by carrying out the reaction in ionic liquids. Quaternary ammonium salts produced in the reaction of *N*,*N*-dimethylaminoethanol with alkyl bromides were used as such media (Scheme 7).

Upon their interaction with DBU, zwitterions are formed initially, which then attack the carbon atom of the CN group of phthalonitrile. The subsequent nucleophilic attack on one of the unsaturated centres of subphthalocyanines results in their opening with formation of intermediate **109**. The final step consists of closure of the macrocycle with formation of the target unsymmetrically substituted phthalocyanines **110**. It was mentioned that intermediates **109** are stable under the reaction conditions. As a result, the yields of the target phthalocyanines reach 60% on the average.

Scheme 7



R = H, Me, Bu^t, NO_2; M = H_2, Zn.

In addition, ionic liquids can repeatedly be used as the reaction media almost without worsening of the results.

It is worth noting, however, that the expansion of the subphthalocyanine macrocycles should be considered as a unusual process, rather than a general preparative method for the synthesis of unsymmetrically substituted monophthalocyanines. First, this approach requires preliminary preparation of subphthalocyanines; second, the high yields of the ring-expansion products were observed in only a limited number of syntheses. Thus, the preparation of monophthalocyanines with the composition $\mathbf{A_3B}$ by cyclization of mixed phthalogens is more advantageous and cheaper.

On the whole, modification of the structure of subphthalocyanine macrocycles opens up great prospects for the synthesis of nano-sized and supramolecular macroheterocyclic compounds.

* * *

Thus, the present review considers methods for the synthesis of different subphthalocyanines as well as their porphyrin analogues. The presence of functional substituents in these macroheterocyclic compounds opens up possibilities for the preparation of unique polynuclear structures. On the basis of numerous physicochemical studies of subphthalocyanines and their analogues, one can conclude that these compounds are promising photo- and electroactive building blocks. Due to specific geometry of the subphthalocyanine macrocycle, multicomponent ensembles can be formed based on these compounds, which can include fullerene fragments in particular. It is hoped that subphthalocyanine-containing systems will find wide use in manufacture of modern materials for optoelectronics and multiterabit storage media in the near future.

The authors thank the staff of the Joint Supercomputer Centre of the Russian Academy of Sciences (www.jscc.ru) for providing computing resources.

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