Porphyrazines: synthesis, properties, application

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The data on the synthesis, properties, and practical application of porphyrazines (tetraazaporphines), the nearest structural analogs of porphyrins and phthalocyanines, have been systematized.

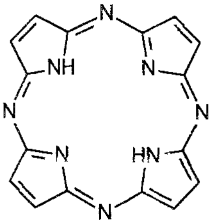
Key words: porphyrazine, phthalocyanine, porphyrin, functional dyes, metal complex catalysis.

Porphyrins and their closest structural analogs belong to a broad class of macroheterocyclic tetrapyrrole systems, which are of considerable interest from scientific and practical viewpoints, because their representatives are components of the most important natural compounds (hemoglobin, myoglobin, cytochromes, chlorophylls, and others) and are involved in such viable processes as photosynthesis, cell respiration, electron transport, *etc.*

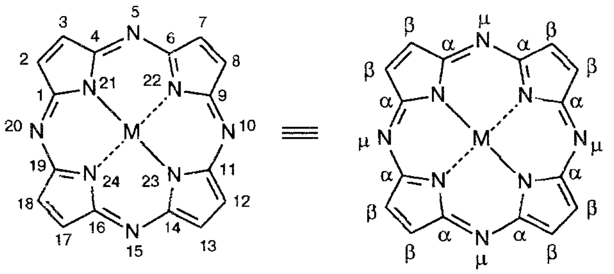
Some synthetic analogs of porphyrins, especially phthalocyanines (Pc), have found wide practical application as dyes and pigments and, recently, in several new fields as well: as bleachable dyes in laser technique, discotic liquid crystals, components of electrochromic and electrophotographic materials, gas sensors, radiation protectors, catalysts of various processes (in particular, electrochemical), antimicrobial drugs, in luminescent diagnostics and photodynamic therapy of cancer tumors, *etc.*[1,2] The development of new fields of technique necessitated the creation of materials with physical and chemical properties different from those of Pc and porphyrins. For example, ecological problems associated with the removal of carbon monoxide in engine exhaust, of nitrogen oxides in the nitrogen fertilizer industry, and of sulfur compounds from oil and natural gases and the technologically important problem of development of processes of mild oxidation of hydrocarbons require the creation of highly efficient and long-lived catalysts. Positive properties of porphyrazines (PA), the closest synthetic analogs of Pc, especially their high stability against oxidation, favor their use in some of the aforementioned areas. PA are considerably less studied than Pc due to the absence of convenient methods for their synthesis. However, recent studies made compounds of this class more accessible.

The purpose of this review is to survey the modern status in the field of synthesis, studies of physical and chemical properties of PA, and their practical application. Some aspects of the chemistry of PA have been reviewed,[3–6] however, the systematic analysis of the available literature concerning all the problems mentioned is lacking.

H_2PA (tetraazaporphine or, according to the IUPAC nomenclature, 2,7,12,17,21,22,23,24-octaazapentacyclo[16,2,1,$1^{3,6}$,$1^{8,11}$,$1^{23,26}$]tetracosaundecaene), in its structure, occupies an intermediate position between other well studied tetrapyrrole macrocyclic systems, porphine and Pc. The conjugation system of the H_2PA molecule is multicontour, and its internal chromophore (without $C^7=C^8$ and $C^{17}=C^{18}$ bonds) contains 18 π-electrons (8 double bonds and 2 p-electrons of internal nitrogen atoms).



H_2PA



MPA

The optimized geometry of the H_2PA molecule[7] points to its considerable similarity with metal-free por-

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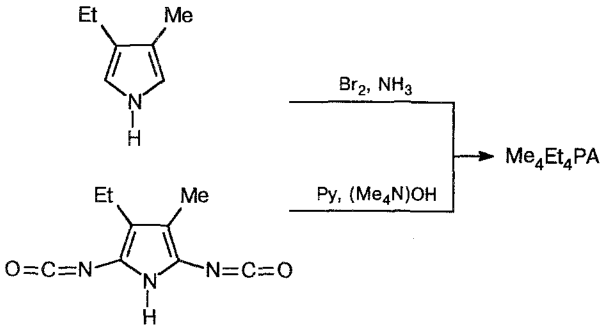
phine (H_2P). Like in H_2P, all C_α—N_μ distances (1.30—1.31 Å) are almost identical. The C_α—C_β bonds are longer (1.44—1.47 Å) than the typical aromatic C—C bond (1.39 Å). The C_α—N—C_α angle at the protonated nitrogen atom is larger (111.2°) than that at the nonprotonated atom (106.9°). The considerable difference between H_2PA and H_2P is that the C_α—N_μ bond in H_2PA (1.31 Å) is much shorter than in H_2P (1.38 Å). This results in a substantial decrease in the central reaction unit in H_2PA compared to that in H_2P. The calculated distances between diagonally opposite central protonated nitrogen atoms are 3.99 and 4.18 Å for H_2PA and H_2P, and those between nonprotonated atoms are 3.86 and 4.04 Å, respectively. This is one of the most important reasons for the distinctions in coordination chemistry and reactivity of these compounds.

The PA ring has amphoteric properties: in acidic media it acts as a base due to μ-nitrogen atoms, while in basic media it manifests acidic properties due to ionization of central imino groups. H_2PA forms complexes with many metals of various groups of the Periodic system of elements.

Synthesis

Attempts have been undertaken to synthesize PA by tetramerization of pyrrole derivatives by analogy with the known syntheses of porphyrins, namely: by reaction of 4-ethyl-3-methylpyrrole with bromine and ammonia or by treatment of 4-ethyl-3-methylpyrrole-2,5-diisocyanate with a mixture of pyridine and tetramethylammonium hydroxide. However, tetraethyltetramethyl-PA has been obtained only in low yields[8,9] (Scheme 1).

Scheme 1



The existing methods for synthesizing PA are based on the tetramerization of derivatives of the corresponding 1,2-dicarboxylic acids, maleonitriles (*Z*-1,2-dicyanoethenes), or their adducts with ammonia, 2-amino-5-iminopyrrolenines. The cyclic system is initially closed to form dehydro-PA, which then is reduced to PA under the reaction conditions.

Various methods for the preparation of metal-PA complexes (MPA) from other PA derivatives or 1,2-dicyanoethenes are known[6,10—12]: (a) fusion of ethene-1,2-dicarbonitriles with metals or their salts, sometimes in the presence of urea; (b) boiling of solutions of ethene-1,2-dicarbonitriles with metals, their salts, or alkoxides (for example, magnesium alkoxide), often in the presence of a catalyst (for example, ammonium molybdate); (c) boiling of an H_2PA solution with metal salts; and (d) boiling of solutions of labile metal complexes of PA (for example, magnesium complex) with metal salts.

Attempts to use 1,2-dicarboxylic acids themselves or some other derivatives (anhydrides, imides, amido and cyano esters, or cyano acids) in the presence of donors of *meso*-nitrogen atoms (urea, ammonia, *etc.*) in syntheses of PA did not result, as a rule, in satisfactory yields of the target products. The only exception is anhydrides or imides of cyclohexene-1,2- and 1,4-dithiacyclohex-2-ene-2,3-carbonitriles or -carboximides with knowingly *cis*-configurations of the carbonyl fragments.[12]

Since the accessibility of substituted PA is determined to a great extent by the accessibility of the starting mono- and disubstituted 1,2-dicyanoethenes, it seems reasonable to consider briefly the methods of their syntheses. Until recently, few syntheses of 1,2-dicyanoethenes were based on the following methods[13]: (a) dehydration of diamides of the corresponding acids, (b) oxidative dimerization of aliphatic mononitriles, and (c) addition to a triple bond of dicyanoacetylene. However, they did not find wide preparative application in the chemistry of PA, because dicyanoacetylene is not easily accessible and is unstable, and undesirable *E*-isomers are formed in all of these methods. In order to synthesize the corresponding substituted PA, more convenient methods for the synthesis of substituted 1,2-dicyanoethenes, using easily accessible starting compounds, have been developed later: (a) substitution of halogen atoms for cyano groups in substituted 1,2-dihaloethenes[14—16] and (b) introduction of substituents into other 1,2-dicyanoethenes already containing the 1,2-dinitrile group by substitution reactions.[14,17]

The reaction of 1,2-dibromobenzenes with copper(I) cyanide, preferable in such solvents as DMF, pyridine, and *N*-methylpyrrolidone (Rosenmund—Brown reaction) has found wide application in syntheses of aromatic *o*-dinitriles, starting compounds for Pc.

Analogous substitution in the haloolefin series is studied to a considerably lesser extent. Some substituted 1,2-dihaloethenes, *viz.*, *Z*- (**1a**) and *E*-1-*tert*-butyl- (**1b**), 1-phenyl- (**2**), 1-(*p*-*tert*-butylphenyl)- (**3**), *E*-1,2-diphenyl-1,2-dibromoethene (**4**), and *E*-1,2-diiodo-1-phenylethene (**5**), have been used as the starting compounds for syntheses of *Z*- and *E*-1,2-dicyanoethenes by this method.[16,17] Dihalides **1—5** were obtained from the corresponding substituted acetylenes by the reactions with bromine upon UV irradiation in hexane or acetic acid in the presence of lithium bromide and with copper(II) bromide or a iodine—potassium iodide mixture in alcohol. *Z*-1,2-Dibromo-1-*tert*-butylethene (**1a**) is formed in ~90 % yield upon photochemical bromination of *tert*-butylacetylene in hexane, while the *E*-isomer is obtained upon the treatment of *tert*-butylacetylene with bromine in acetic acid in the presence of lithium bromide.[18] The analysis shows that dibromides **2—4** are the mixtures of *Z*- and *E*-isomers, the former being predominant. Halogen atoms were replaced with cyano groups by the reactions of dihalides with CuCN in DMF or *N*-methylpyrrolidone at 160—180 °C.[14,15]

$$\underset{\mathbf{1-5}}{\mathrm{RCX{=}CXR'}} \xrightarrow[\text{DMF}]{\text{CuCN}} \underset{\mathbf{6-9}}{\mathrm{RC(CN){=}C(CN)R'}}$$

R = H, R′ = $\mathrm{Bu^t}$ (**1**, **6**), Ph (**2**, **5**, **7**), *p*-$\mathrm{Bu^tC_6H_4}$ (**3**, **8**);
R = R′= Ph (**4**, **9**); X = Br (**1—4**), I (**5**)

The dinitrile—monovalent copper complex formed in the reaction is decomposed by treatment with aqueous ammonia. *Z*-Dibromide **1a** yielded 63 %, and *E*-dibromide **1b** yielded only 24 % of *Z*-1-*tert*-butyl-1,2-dicyanoethene (**6**).[15] Only arylmaleonitriles (**7**, **8**) are formed from dihalides **2**, **3**, and **5**, independently of configurations, while *E*-dibromide **4** gives only diphenylfumaronitrile (**9**).

The photochemical isomerization of *E*-1,2-dicyano-1-R-2-R′-ethenes (R = R′ = Et; R = Bu, R′ = H; R = Ph, R′ = H) in acetonitrile resulting in the corresponding *Z*-dinitriles in 48—57 % yields[16] is described, as well as the isomerization of fumaronitrile to maleonitrile under the action of butyllithium in hexane.[19]

The presence of electron-accepting cyano groups in mono- and dichloromaleo(fumaro)nitrile molecules facilitates considerably nucleophilic substitution reactions of chlorine atoms (synartetic acceleration). For example, the reaction of a mixture of monochlorides (*Z* : *E* = 2.5 : 1) or individual isomers with sodium *tert*-butyloxide or *tert*-pentylthiolate results in the formation only of *cis*-isomers, *tert*-butoxy- (54 %) and *tert*-pentylthiomaleonitriles (42 %).[17] *tert*-Butylamino-, diethylamino-, and allylaminomaleonitriles were obtained by amination of these compounds. It is supposed that the substitution of the chlorine atom occurs here according to the addition—elimination scheme. The corresponding 1,2-dicyanoethenes with fluorine-containing substituents were obtained in a similar way from *Z*,*E*-1-chloro-1,2-dicyanoethene and sodium hexafluoroisopropoxide, phenylbis(trifluoromethyl)methoxide, or pentafluorophenolate in acetonitrile.[20]

The reactions of nucleophilic substitution of chlorine atoms in a mixture of dichloromaleo- and dichlorofumaronitrile (1 : 1) were used for preparing 1,2-dicyanoethenes with two identical substituents in a molecule. For example, the condensation of this mixture with sodium *tert*-pentylthiolate results in the formation of a 3 : 1 mixture of *Z*- and *E*-1,2-dicyano-1,2-di(*tert*-pentylthio)ethene in 30 % yield, and *tert*-butylamine gives a mixture of *Z*- and *E*-1,2-bis(*tert*-butylamino)-1,2-dicyanoethene in a 2 : 3 ratio. Only monosubstitution products, a mixture of *Z*- and *E*-1-chloro-1,2-dicyano-2-ethoxyethene (3 : 2), were formed in the reaction with sodium ethoxide. By analogy, in the reaction with sodium pentafluorophenolate only one chlorine atom is replaced to form 1-chloro-2-pentafluorophenoxy-1,2-dicyanoethene in 50 % yield along with the product of reduction of the chlorine atom in the latter, 1-pentafluorophenoxy-1,2-dicyanoethene.[20]

Other methods have been also suggested for the preparation of 1,2-dicyanoethenes, for example, the reaction of malononitrile with cyanoanhydrides of pivalic and benzoic acids in the presence of β-alanine as a catalyst, according to Knoevenagel.[21] The oxidation by bromine in pyridine of the products of addition of hydrogen cyanide to the corresponding benzilidenemalononitriles has been used to synthesize tricyanoethenes with certain fluorine-containing substituents.[22]

$$\mathrm{RCH{=}C(CN)_2} \xrightarrow[\mathrm{H^+}]{\mathrm{KCN}} \mathrm{RCH(CN){-}CH(CN)_2} \xrightarrow[\mathrm{Py}]{\mathrm{Br_2}}$$
$$\longrightarrow \mathrm{RC(CN){=}C(CN)_2}$$

R = *o*-$\mathrm{CF_3C_6H_4}$, *o*-$\mathrm{CF_3CHFCF_2OC_6H_4}$,
p-$\mathrm{CHF_2CF_2CH_2N(Et)C_6H_4}$, $\mathrm{C_6F_5}$

Tricyanovinylation is convenient for preparing some tricyanoethenes. For example, the reactions of *N*,*N*-dialkylanilines (Alk = Me, Et, or Bu) with tetracyanoethene (TCE) in DMF at 20—25 °C result in the formation of the corresponding 1,1,2-tricyano-2-(*p*-dialkylaminophenyl)ethenes in high yields.[13] 2-(*tert*-Butylamino)-1,1,2-tricyanoethene is formed from TCE and *tert*-butylamine in 46 % yield.[21] Tricyanoethenes are convenient for preparing PA, because these molecules *a fortiori* contain *cis*-dinitrile groups. With $\mathrm{N_2O_4}$ in chloroform at 20—25 °C, phenyl- and *p*-*tert*-butylphenylmaleonitrile form addition—elimination products, 1-nitro-2-phenyl- and 2-(*p*-*tert*-butylphenyl)-1-nitro-1,2-dicyanoethenes.[23]

$$\mathrm{RC(CN){=}CHCN} \xrightarrow{\mathrm{N_2O_4}} \mathrm{[RC(NO_2)(CN)CH(NO_2)CN]} \xrightarrow{\mathrm{-HNO_2}}$$
$$\longrightarrow \mathrm{RC(CN){=}C(NO_2)CN}$$

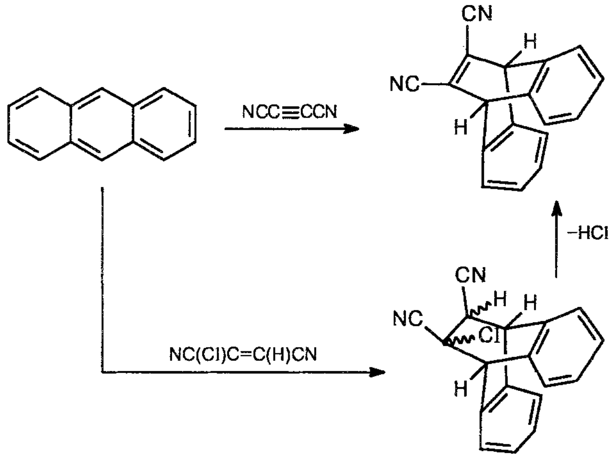
R = Ph, $\mathrm{Bu^tC_6H_4}$

The 1,2-addition of 1-R-azulene (R = H or Me) to dicyanoacetylene in tetrachloroethane at 0—5 °C results in the formation of 1,2-dicyano-1-(3-R-azulenyl)ethenes.[14] Di(4-R-phenyl)maleonitriles were obtained by the oxidative dimerization of 4-R-benzyl cyanides (R = H or $\mathrm{Bu^t}$) by the action of sodium methoxide and iodine in a methanol—ether mixture.[24,25] 2,3-Dicyano-5-R-1,4-dithiacyclohex-2-enes, the starting compounds for the preparation of 4,5:7,9:14,15:19,20-[*a*,*i*,*h*,*s*]-

tetrakis(dithiacyclohexeno)-PA,[26] have been obtained by the condensation of 1,2-dibromoethenes with sodium *Z*-1,2-dicyanoethenedithiolate, which is the product of the reaction between carbon disulfide and sodium cyanide in ethanol. 2,3-Dicyano-1,4-dithiacyclohex-2-ene was also synthesized by the condensation of dichloromaleo(fumaro)nitrile with sodium dithioglycolate.[14] The synthesis of bis(dialkylamino)maleonitriles by alkylation of maleonitrile (tetramer of hydrogen cyanide) is known.[27]

2,3-Dicyano[5,6:7,8]dibenzobarrelene,[28,29] which was obtained in a nearly quantitative yield upon Diels—Alder condensation of anthracene with dicyanoacetylene at 120 °C[30] (Scheme 2) or dehydration of the corresponding diamide by thionyl chloride in DMF, has also been used in the synthesis of PA. Diamide was obtained upon treatment of the corresponding ester, the Diels—Alder adduct of anthracene with dimethyl acetylenedicarboxylate, with ammonia. A simplified method for the synthesis of this compound in a more than 70 % yield has also been suggested: the condensation of anthracene with the more easily accessible and stable chloromaleo(fumaro)dinitrile at 180—200 °C *via* the intermediate stage of formation of the adduct followed by the elimination of hydrogen chloride.[31]

Scheme 2



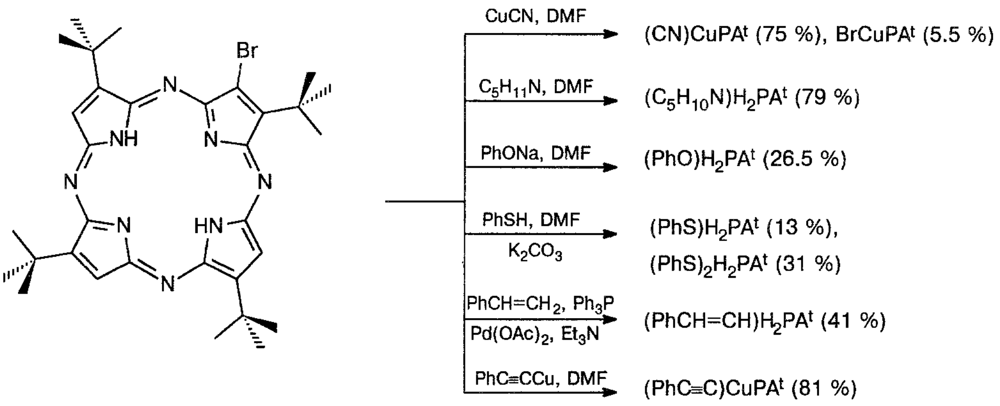
In addition to tetramerization of maleonitriles, PA derivatives can be also obtained by substitution of hydrogen atoms or other substituents in the macrocycle. For example, the bromination of H_2PA with bromine or its complex with dioxane in acetic acid gives 2,7,12,17-tetrabromo-H_2PA.[32] The same compound is formed in 40 % yield in the reaction of MgPA with bromine in acetic acid at 20—25 °C. Metal complexes of PA (MPA, where M = Mg, Zn, Cd, Cu, Ni, Co, or Cr) were synthesized by the reaction of H_2PA with salts of the corresponding metals.[33] The chlorination of H_2PA by thionyl chloride at 40—45 °C or sulfuryl chloride (20—25 °C) results in the formation of tetrachloro-substituted derivatives in 53 and 43 % yields, respectively.[34] H_2PA and its copper complex react with chlorosulfonic acid to form sulfonyl chlorides, hydrolysis of which gives the corresponding sulfonic acids.[35] Some substitution reactions in octaphenylporphyrazines are described. The chloromethylation of the metal-free compound by a mixture of chlorosulfonic acid, paraform, and sodium chloride (1 : 5 : 1) at 0—6 °C results in the formation of octa(*p*-chloromethylphenyl)-PA, whose reaction with pyridine gives a water-soluble pyridinium salt.[35] Water-soluble aluminum complex of octa(*p*-sulfophenyl)-PA was obtained by sulfonation of bromoaluminum complex with oleum.[36]

Tetrakis(*tert*-butyl)-PA (PA^t), in which four bulky *tert*-butyl groups provide higher solubility of both the initial compounds and the reaction products in low-polar organic solvents (hexane, benzene, chloroform, *etc.*) and reduce the number of possible reaction centers to 4, is a convenient starting compound for the synthesis of substituted PA. The reaction of equimolar amounts of H_2PA^t and *N*-bromosuccinimide (NBS) in chloroform at 20—25 °C results in a mixture of 47 % of monobromo- and 22 % of dibromo-substituted derivatives.[37] An increase in the amount of NBS results in the formation of products with a higher substitution degree: the yield of the product of complete substitution, tetrabromide, is ~80 % with the 10—20-fold amount of NBS. H_2PA and its complexes with Cu^{II} and Co^{II} were nitrated with mixtures of fuming nitric and acetic acids, nitronium tetrafluoroborate in sulfolane, and dinitrogen tetraoxide in hexane.[38] Di-, tri-, and tetranitro-H_2PA^t are formed in 26, 23, and 37 % yields, respectively, when H_2PA^t has been nitrated by a 1 : 1 mixture of fuming nitric and glacial acetic acids at 0 °C for 3—5 min. An increase in the reaction time results in the formation of a mixture, the tetra-substituted derivative predominated. Mononitro-H_2PA^t was obtained in 6 % yield only in the nitration by 2% nitric acid in acetic acid. The nitration of $Co^{II}PA^t$ results only in the formation of the tetranitro-substituted derivative in 52 % yield, and that of $Cu^{II}PA^t$ results in the formation of a mixture of tri- and tetranitro-$CuPA^t$ in 14 and 45 % yields, respectively.

The synthesis of PA derivatives by substitution of halogen atoms in a PA molecule has been described.[37] The reactions of monobromo- and dibromo-PA with CuCN in DMF result in the formation of copper complexes of mono- and dicyano-PA; the latter was chromatographically separated into two isomers with cyano groups at adjacent and opposite pyrrole rings (Scheme 3).

The nucleophilic substitution of the bromine atom in monobromo-PA^t results in the corresponding monosubstituted PA^t (see Scheme 3). For example, the reaction of monobromo-H_2PA^t with copper phenylacetylenide under cyanation conditions results in the formation of phenylethynyl-$CuPA^t$ in a high yield, while the reaction with styrene in the presence of triethylamine and palladium catalyst results in the formation of styryl-H_2PA^t.[37]

Scheme 3



However, the disubstituted product is also formed due to secondary reactions in the case of thiophenol. The first representative of covalently linked bridged dimeric PA was obtained from monobromo-PA^t and 2,2-bis(*p*-hydroxyphenyl)propane.

The complete or partial substitution of halogen atoms for pentyloxy groups has been also observed in the condensation of mono- and dichloromaleo(fumaro)nitrile with magnesium pentoxide.

An unusual transformation has been observed in the octakis(dialkylamino)-PA series. A compound with the long-wave band shifted to the red region has been isolated as an admixture in the synthesis of octakis(dimethylamino)-MgPA. This compound has been also obtained in a high yield, when octakis(dimethylamino)-MgPA is treated with acetic acid in air.[39] The structure of octakis(dimethylamino)-2-secoporphyrazine-2,3-dione formed due to the oxidation of the double bond of one of the pyrrole rings by the singlet oxygen has been assigned to this compound on the basis of the data of elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and X-ray diffraction analysis.

Spectral properties

Electronic absorption spectra (EAS) of PA play an important role in their practical use. Tetraazasubstitution in a porphine molecule does not result in a change in the number of π-electrons, *i.e.*, molecular systems of porphine and PA are isoelectronic. The four-band spectrum of porphyrins in the 450—650 nm range is transformed into a two-band one on going to PA, which is attributed to lifting off of the quasi-forbiddance of bands I and III; this results in an increase in their intensities and decrease in those of bands II and IV. The long-wave range of EAS of H$_2$PA contains two bands at 617 and 547 nm (in chlorobenzene), which represent the split Q band (according to the common classification of porphyrin bands).[40] The introduction of *tert*-butyl groups or dibenzobarrelene moieties into a PA molecule exerts no substantial effect on EAS; however, an increase in the solubility of PA in low-polar solvents (hexane, benzene) provides the possibility of studying them in a wider spectral range.[15,28] For example, H$_2$PA^t in hexane has a distinct resolution of the Q band, which is absent in chlorobenzene. Metal complexes of PA and porphyrins exhibit the fusion of two long-wave bands into one band due to an increase in the symmetry of the molecule from D_{2h} to D_{4h}. This band exhibits the hypsochromic shift by ~100 nm compared to the spectrum of Pc. Bands of low intensity, which are vibrational satellites of the Q band, appear in the 530—550 nm range. The position of the Q band of MPA^t depends on the nature of the central metal atom and varies from 570 nm for Co^{II}PA^t to 620 nm for Pb^{II}PA^t. Its intensity depends on the solvent. The molar extinction coefficient of MgPA^t is $4.8 \cdot 10^4$ and $1.23 \cdot 10^5$ L mol^{-1} cm^{-1} in pyridine and hexane, respectively.

A broad intense band B (related to the Soret band of porphyrins) and less intense bands N and L are observed in the near-UV range of the spectrum (~330 nm). The shape and intensity of band B depend substantially on the nature of the central metal atom, and the band is splitted in some cases, which is rationalized as the superposition of $d_\pi \rightarrow \pi^*$ type bands.

The character of the curve of the magnetic circular dichroism spectrum of H$_2$PA^t in the region of the Q band, whose peaks correspond exactly to the maxima in the absorption spectrum, allows one to assign it to the Faraday B term, because the excited state of H$_2$PA^t is not degenerate.[5] On the contrary, the S-like character of the Q band of MPA^t (M = Mg, Cu, or VO) testifies in favor of the Faraday A term, because their excited states are twice degenerate. Nevertheless, the real A term is observed only for octaphenyl-MgPA with more perfect symmetry D_{4h}, and the deviations from the symmetry for *tert*-butyl-substituted PA is associated with the fact that the latter exist as a mixture of position isomers.

EAS of dibenzobarrelene analogs of PA in solutions and crystalline films are very similar, which is caused by the weakening of the intermolecular interaction in the crystalline state due to steric hindrances exerted by bulky dibenzobarrelene moieties.[28]

Quantum-chemical calculations of a PA molecule and several of its metal complexes have been performed by various methods,[40—45] including the *ab initio* self-consistent field method, taking into account all electrons.[7] According to the calculation performed by Gouterman and co-workers by the extended Hückel method taking into account valent electrons,[42] the Q band in EAS of MPA is caused by the $a_{1u}(\pi)\rightarrow e_g(\pi^*)$ transition. The a_{1u} orbital is mainly composed of the orbitals of α-C atoms of pyrrole rings with a noticeable contribution of the atomic orbitals of β-C atoms. The B band is related to the $a_{2u}(\pi)\rightarrow e_g(\pi^*)$ transition, and the a_{2u} orbital consists almost exclusively of the atomic orbitals of pyrrole and μ-nitrogen atoms. The B bands of PA and Pc are broadened, which is caused by the superposition of σ—π*-type bands. The lower unoccupied molecular orbital (LUMO) e_g covers the whole molecule, predominantly the atoms of the inner 16-membered ring. The spectral effect of *meso*-aza-substitution in a porphine molecule is accounted for its different influence on higher occupied MO: the ionization potential of the a_{1u} MO changes only slightly (0.3 eV), while it is considerably higher (by ~2.2 eV) for the a_{2u} MO of PA than that of porphyrins.[7]

Higher solubility of PA^t (in methyl methacrylate) made it possible to introduce them into polymeric films; they tend to form ordered structures of the Langmuir—Blodgett-type films. A hidden band at 600—650 nm was observed in the spectrum of H_2PA^t by Stark spectroscopy. This band almost coincides with the electronic band, whose formation is related to the charge transfer between different layers of the Langmuir film.[46]

The introduction of four or eight methyl groups into a molecule of nonsubstituted PA results in some (~15 nm) shift of the Q band.[11,47,48] The shift is greater for octaphenyl-PA [25] due to the partial conjugation of the phenyl rings with the macroring π-system. Octakis(*p*-*tert*-butylphenyl)-PA with higher solubility in organic solvents than octaphenyl-PA is especially convenient for spectral studies.[24] The introduction of four alkylamino (*tert*-butylamino, diethylamino, or allylamino),[17] alkoxy (*tert*-butoxy or pentyloxy), or alkylthio (methylthio or *tert*-pentylthio)[17,49] groups into a PA molecule results in a considerable bathochromic shift of the Q band, which reaches 130 nm for alkylamino-derivatives. Such a strong shift occurs due to the conjugation of unshared electron pairs of substituents with the π-system of the macroring. Broadening of the Q band in these compounds compared to nonsubstituted analogs is likely related to the appearance of spectral nonidentity of positional isomers in PA. This can be confirmed by EAS of magnesium tetrakis(*tert*-butylamino)-PA in a vitrifying matrix at 77 K, which contains two intense and resolved bands at 732 and 767 nm assigned to individual isomers or groups of isomers.

In the case of magnesium-*tert*-pentylthio-substituted PA, the bathochromic shift of the Q band is only 2 nm on going from tetra- to octa-substituted PA, while the spectrum of magnesium-octakis(*tert*-butylamino)-substituted PA exhibits even the 87-nm hypsochromic shift, which is related to steric hindrances disturbing the interaction of these groups with the macroring of PA.[17] In fact, in octamethylthio- and dithiacyclohexeno-PA, in which steric effects are not so strongly expressed, Q bands are bathochromically shifted compared to tetraalkylthio-substituted analogs.[49,50] The synthesis of octakis(dialkylamino)-PA by tetramerization of the corresponding bis(dialkylamino)maleonitriles with magnesium propoxide in propanol has been recently described.[27] The maximum of the Q band in the spectrum of octakis(dibenzylamino)-PA in dichloromethane is localized at 707 nm.

Such electron-accepting substituents as cyano, carboxyl,[51] ethoxycarbonyl,[14] and nitro[38] groups as well as chlorine[48] and bromine[37] atoms in the macroring of PA result in the bathochromic shift of Q (up to 30 nm) and B (up to 20 nm) bands.

The Q band in the spectrum of $ZnPA^t(NO_2)_3$ is splitted into two components spaced 540 cm^{-1} apart and mutually perpendicularly polarized, as follows from the polarization spectrum. This testifies that pyrrole rings with and without nitro groups are considerably nonequivalent. In the EAS of nitro-derivatives of H_2PA^t, the splitting Q_1—Q_2 decreases and the intensity of the B band increases compared to those of nonsubstituted H_2PA^t. In the case of vanadyl-tetrakis(*tert*-butyl)tetracyano-PA, two fractions were isolated by chromatography. Judging from the spectra, they differ in the degree of symmetry of the molecules.[37] The Q band in the EAS of copper-monocyano-PA^t is present as a doublet (602 and 574 nm in benzene) due to the decrease in symmetry of the molecule compared to the tetracyano-substituted analog. The spectrum of copper-dicyano-substituted PA^t depends on the mutual arrangement of cyano groups in the macrocycle: a single band at 598 nm and a doublet at 627 and 563 nm for isomers with adjacent and opposite arrangements of the cyano groups, respectively.

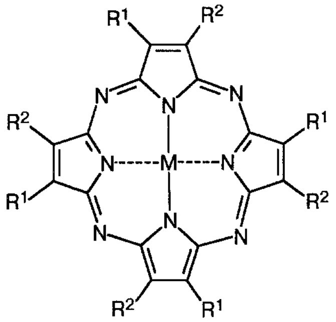
Unusual hypsochromic shifts of the Q and B bands to 564 and 300 nm (in chloroform) are observed in the spectrum of copper-octabenzoyl-PA^t.[14] The introduction of fluoro-containing substituents into a PA molecule also often results in the hypsochromic shift of the Q band compared to other electron-accepting substituents. For example, the spectrum of tetraphenyltetracyano-MgPA contains the Q band at 666 nm, while in the corresponding pentafluorophenyl analog the Q band is at 634 nm (in chloroform).[20]

The simultaneous existence of four electron-donating and four electron-accepting substituents in a PA molecule results in a substantial change in the EAS.[51] For example, when *tert*-butylamino or *p*-dialkylaminophenyl groups are introduced along with cyano groups, the value of the shift of the Q band is up to 300 nm, which is related to the extension of the conjugation system of a chromophore analogous to that observed for merocyanine dyes.

The EAS of the most typical representatives of PA are listed in Table 1. The more detailed data published before 1988 are given in the catalog.[52]

Luminescent properties of PA, unlike those of porphyrins and Pc, are studied rather poorly. It is shown by the example of PA^t that the fluorescence quantum yields of the metal-free compound and zinc complex are considerably lower (Table 2) than those of the corresponding Pc, and the fluorescence spectrum is the mirror reflection of the absorption spectrum.[54] Fluorescence

Table 1. Electronic absorption spectra of several porphyrazines



M	R^1	R^2	Solvent	λ_{max}/nm (logε) [relative intensity]	Ref.
HH	H	H	PhCl	617 (4.75), 545 (4.60), 333 (4.70)	10
Mg	H	H	MeOH	584 (5.03), 536 (4.18), 326 (4.79), 228 (4.26)	10
Ni^{II}	H	H	o-$C_6H_4Cl_2$	577 (4.85), 530 (4.20), 345 (4.57), 314 (4.44)	10
Cu^{II}	H	H	o-$C_6H_4Cl_2$	578 (4.98), 531 (4.13), 334 (4.57)	10
HH	Me	H	PhCl	624 (4.90), 596 (3.99), 552 (4.71), 341 (4.71)	47
Cu^{II}	Me	H	PhCl	585 (5.03), 536 (4.25), 339 (4.82)	47
HH	Me	Me	PhCl	627 (4.86), 597 (3.94), 556 (4.66), 343 (4.89)	11
Cu^{II}	Me	Me	PhCl	593 (5.02), 542 (4.19), 343 (4.83)	11
HH	Et	Et	CH_2Cl_2	627 (4.8), 600 (3.9), 558 (4.6), 515 sh, 349 (4.9)	16
HH	$—CH_2(CH_2)_2CH_2—$		PhCl	628 (4.79), 600 (3.99)	49
Cu^{II}	$—CH_2(CH_2)_2CH_2—$		o-$C_6H_4Cl_2$	591 (5.05), 541 (4.24), 343 (4.81)	49
HH	Bu^t	H	Hexane	620 (5.00), 583 (3.96), 568 (4.00), 547 (4.79), 521 s (4.03), 333 (4.90)	15
Mg^{II}	Bu^t	H	Hexane	591 (5.24), 542 (4.35), 333 (4.94)	15
V^{IV}O	Bu^t	H	Hexane	594 (5.09), 543 (4.19), 342 (4.76)	15
Co^{II}	Bu^t	H	Hexane	570 (4.85), 520 s (4.19), 332 sh (4.58), 315 (4.64)	15
Ni^{II}	Bu^t	H	Hexane	576 (4.75), 556 (4.21), 530 (4.04), 340 (4.40), 305 (4.53)	15
Cu^{II}	Bu^t	H	Hexane	581 (5.15), 533 (4.30), 336 (4.83)	15
Zn^{II}	Bu^t	H	Hexane	592 (5.23), 543 (4.33), 336 (4.97)	15
Pd^{II}	Bu^t	H	Hexane	572 (5.17), 553 (4.50), 525 (4.35), 336 (4.74), 299 (4.49)	15
HH	9,10-H_2-Anthrylene		C_6H_6	638 (4.97), 560 (4.40), 417 (4.08), 373 (4.43)	28
Cu^{II}	9,10-H_2-Anthrylene		C_6H_6	586 (5.08), 539 (4.21), 501 (3.57), 4.20 (4.15), 364 (4.62)	28
Mg	Ph	Ph	Py	636, 585, 378	53
HH	Bu^tC_6H_4	Bu^tC_6H_4	Heptane	666 (4.90), 595 (4.69), 562 sh (4.34), 450 (4.51), 362 (4.97), 268 (4.53)	25
Cu^{II}	Bu^tC_6H_4	Bu^tC_6H_4	Heptane	625 (5.00), 575 (4.36), 450 (4.40), 360 (4.88)	25
V^{IV}O	Cl	H	$CHCl_3$	606 (4.79), 552 (4.25), 350 (4.51)	48
V^{IV}O	Cl	Cl	$CHCl_3$	612 (4.69), 583 sh (4.04), 556 (3.74), 346 (4.42)	48
HH	Br	H	$CHCl_3$	639, 572	32
Cu^{II}	Br	H	Py	605 (4.90), 565 (4.33), 359 (4.83)	33
HH	Cl	H	$CHCl_3$	638, 572	34

Table 1 (*continued*)

M	R^1	R^2	Solvent	λ_{max}/nm (logε) [relative intensity]	Ref.
HH	Br	Bu^t	C_6H_6	636 (4.82), 566 (4.62), 344 (4.66)	37
HH	O_2N	Bu^t	$CHCl_3$	632 (4.87), 604 (4.01), 563 (4.71), 530 sh (4.17), 341 (4.85)	38
Co^{II}	O_2N	Bu^t	$CHCl_3$	577 (4.84), 528 (4.36), 317 (4.68)	38
Cu^{II}	O_2N	Bu^t	$CHCl_3$	588, 536, 338 [1.0:0.20:0.53]	38
HH	Bu^tO	H	$CHCl_3$	646 (4.60), 594 (4.46), 574 sh (4.26), 331 (4.82)	17
Mg	Bu^tO	H	$CHCl_3$	612 (4.67), 565 (4.25), 340 (4.82)	17
Mg	$(CF_3)_2CHO$	H	Hexane	595, 351	20
HH	$PhC(CF_3)_2O$	H	Hexane	624, 592, 550, 326 [1.0:0.72:0.74:1.83]	20
Cu^{II}	$PhC(CF_3)_2O$	H	Hexane	590, 582, 536 sh, 328 [1.0:0.97:0.36:1.19]	20
HH	C_6F_5O	Cl	Hexane	628, 558, 390 sh, 334 [1.0:0.91:0.50:2.29]	20
Mg	C_6F_5O	Cl	Hexane	600, 560 s, 440 sh, 342 [1.0:0.20:0.31:1.84]	20
Mg	$EtMe_2CS$	H	$CHCl_3$	649 (4.74), 350 (4.89)	17
HH	MeS	MeS	PhCl	709 (4.54), 637 (4.41), 515 (4.30), 367 (4.63)	49
Cu^{II}	MeS	MeS	PhCl	667 (4.68), 610 (4.30), 497 (4.17), 363 (4.56)	49
Mg	Bu^tNH	H	$CHCl_3$	740 (4.49), 710 (4.84), 642 sh (4.37), 466 (4.22), 336 (5.12)	17
Mg	$CH_2=CHCH_2NH$	H	$CHCl_3$	686 (4.81), 460 (4.19), 345 (4.98)	17
Mg	Et_2N	H	$CHCl_3$	716 (4.72), 646 sh (4.49), 462 (4.36), 338 (4.99)	17
Mg	Bu^tNH	Bu^tNH	$CHCl_3$	623 (4.95), 571 sh (4.26), 346 (5.08)	17
Mg	$(PhCH_2)_2N$	$(PhCH_2)_2N$	CH_2Cl_2	707 (4.51), 574 (4.45), 368 (4.75)	
Cu^{II}	Bz	Bz	$CHCl_3$	564 (4.41), 300 (4.89)	14
$V^{IV}O$	HOOC	Bu^t	$CHCl_3$	602 (5.02), 546 (4.19), 346 (5.00)	51
HH	CN	Bu^t	$CHCl_3$	650 (4.98), 576 (4.76), 540 (4.11), 352 (4.94)	51
Cu^{II}	CN	Bu^t	$CHCl_3$	606 (5.12), 552 (4.52), 352 (4.99)	51
Mg	CN	Ph	$CHCl_3$	666 (4.84), 600 (4.26), 380 (4.88)	51
Mg	CN	C_6F_5	$CHCl_3$	634 (4.86), 518 (4.04), 373 (4.64)	22
Cu^{II}	CN	C_6F_5	$CHCl_3$	625 (4.86), 572 (4.22), 364 (4.61)	22
Mg	CN	$o\text{-}CF_3C_6H_4$	$CHCl_3$	624 (5.08), 570 (4.37), 336 (4.92)	22
Mg	CN	$Me_2NC_6H_4$	$CHCl_3$	834 (4.53), 636 (4.22), 534 (4.01), 408 (4.54)	51
HH	CN	Bu^tNH	DMF	774 (4.68), 712 (4.60), 682 (4.42), 648 (4.30), 450 (4.26), 400 (4.24), 334 (4.91)	51
Mg	CN	Bu^tNH	$CHCl_3$	756 (4.72), 654 (4.29), 402 (4.21), 338 (4.92)	51
Cu^{II}	CN	Bu^tNH	$CHCl_3$	729 (4.91), 662 (4.36), 490 (4.19), 396 (4.25), 324 (4.81)	51
HH	HO_3S	H	Py	636 (4.73), 577 (4.58), 369 (4.80)	35
Cu^{II}	HO_3S	H	Py	629 (4.86), 570 (4.22), 366 (4.56)	35

Table 2. Spectral luminescent properties and rate constants of transitions of some PA in EPE at 77 K

Substance	λ_A^{00}	λ_F^{00}	λ_P^{00}	$\Delta E_{S_1T_1}/cm^{-1}$	φ_F	τ_F/ns	$\varphi_P \cdot 10^5$	τ_P/ms	$k_P \cdot 10^2$	k_{TS}	$k_F \cdot 10^{-7}$	$k_{ST} \cdot 10^{-8}$
	/nm								/s^{-1}			
H_2PA^t	615	618	965	5820	0.18	3.0	0.31	1.4	0.27	710	6.0	2.7
$H_2PA^t(NO_2)_2$	616	619	955	5700	0.14	1.9	0.17	1.2	0.16	833	7.4	4.5
$H_2PA^t(NO_2)_3$	612	615	982	6080	0.12	1.7	0.46	1.1	0.45	870	7.1	5.2
$H_2PA^t(NO_2)_4$	621	629	977	5670	0.16	1.2	0.49	0.9	0.65	1100	13.0	7.0
$ZnPA^t$	591	595	923	5970	0.28	2.8	130.0	2.9	62.0	340	10.0	2.6
$ZnPA^t(NO_2)_3$	603	608	920	5580	0.26	2.9	90.0	2.9	43.0	340	9.0	2.6

Note. EPE is a 5 : 5 : 2 ethyl ether—light petroleum—ethanol mixture; φ_F is the fluorescence quantum yield at 293 K in toluene; τ_F is the fluorescence lifetime at 293 K; φ_P is the phosphorescence quantum yield; τ_P is the phosphorescence lifetime; k_P and k_F are the rate constants of radiative transitions $T_1 \rightarrow S_0$ and $S_1 \rightarrow S_0$; k_{TS} and k_{ST} are the rate constants of nonradiative conversion and intersystem crossing, respectively.

and phosphorescence spectra of several nitro-substituted PA^t have been also studied. The introduction of nitro groups into the $ZnPA^t$ molecule results in certain increase in the intensity of vibronic bands in both fluorescence and phosphorescence spectra and only in the fluorescence spectrum of the metal-free compound. It is shown that the fluorescence quantum yield depends weakly on the number of nitro groups in the PA molecule, especially for zinc complexes for which the duration of fluorescence remains almost unchanged as well.

The *meso*-aza-substitution in a porphine molecule results in a shift to higher frequencies of bending out-of-plane vibrations of C—H groups of pyrrole moieties in the IR spectrum: from 772 cm^{-1} for porphine to 803 cm^{-1} for metal-free PA.[55] Like in porphine, planar bending vibrations (δCH) of H_2PA appear in the 900 to 1200 cm^{-1} region, and skeleton vibrations of C—N bonds appear at 1350—1550 cm^{-1}. The frequency of symmetric stretching vibrations of the N—H bond (νNH) at 3305 cm^{-1} is the measure of its ionization and testifies that H_2PA is more acidic than porphyrins.

The IR spectrum of the adduct of H_2PA with pyridine[56] exhibits vibrations at 1953 and 2012 cm^{-1} assigned to the $C{=}NH^+$ groups of pyridine hydrochloride and no νNH band, which indicates that the N—H bond of PA is completely ionized even under the action of a weak base. True shape of spectra of the majority of PA studied is distorted by additional bands assigned to intermolecular aggregates. Bulky *tert*-butyl substituents or dibenzobarrelene moieties in a PA molecule prevent aggregation, which appears in their IR spectra.[5,57] In order to estimate qualitatively the relative stability of the metal—ligand bond in the series of dibenzobarrelene analogs of PA, the band at 1550 cm^{-1} sensitive to metal substitution has been studied: its frequencies are equal to 1488, 1502, 1508, and 1517 cm^{-1} for magnesium, copper(II), cobalt(II), and nickel(II) complexes, respectively. The IR spectrum of MPA, like that of PcM, contains another spectral region near 1000 cm^{-1} sensitive to metal substitution. The band shifts from 993 cm^{-1} for the lead complex to 1020 cm^{-1} for the palladium complex.

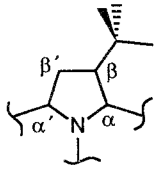
^1H, ^{13}C, and ^{15}N NMR studies showed the existence of an intramolecular exchange process (fast migration of protons between nitrogen atoms of central amino groups) in the porphyrin series. At low temperatures, two imino protons are localized in the opposite pyrrole rings in the prompt-rigid porphyrin structure.

The analysis of the ^1H NMR spectra (100 MHz) of H_2PA^t in carbon disulfide indicates that the fast N—H proton exchange occurs at 20—25 °C, which becomes slow in the NMR time scale at −88 °C.[58] The separate signals for β-protons (8.69 and 9.08 ppm) and protons of *tert*-butyl groups (2.15 and 2.25 ppm) that belong to pyrrolenine and pyrrole rings, respectively, are registered. As in the case of porphyrins, the signal for β-protons of the pyrrole rings containing imino protons lies in a lower field and is additionally broadened by 1.8 Hz due to the spin-spin coupling with the latter. The character of the spectrum (only two signals for β-protons and protons of *tert*-butyl groups in the absence of exchange) is consistent with the molecular symmetry of H_2PA^t. The signals for *tert*-butyl groups collapse at −79 °C, while the signals for β-protons collapse at −69 °C. The shape of the signal for the imino protons remains unchanged, as can be expected from the symmetry of the molecule. It considerably shifts downfield (from −2.87 to −2.59 ppm) as the temperature increases from −88 to 30 °C, which is explained by the formation of sandwich type intermolecular aggregates in the solution. The comparison of the values of the free activation energy of proton exchange (9.9 kcal mol^{-1} for H_2PA^t and 11—12 kcal mol^{-1} for porphyrins) testifies that the aza-substitution results in an increase in the migration rate of the imino protons.

The ^{13}C NMR spectra of H_2PA^t in deuteriochloroform and trifluoroacetic acid were studied, using TMS as an internal standard (Table 3).[59] The signal of the C_β atom directly bonded to the proton is the most intense due to the Overhauser effect, and the signals of the C_α and $C_{\alpha'}$ atoms are slightly broadened, which is explained by N—H-tautomerism.

The signals for the C_α and $C_{\alpha'}$ atoms lie in a lower field due to the substantial effect of the nitrogen atoms. The $C_{\beta'}$ atom resonates in a lower field than C_β due to the effect of the *tert*-butyl group. Small downfield and upfield shifts of the signals for the $C_{\beta'}$ and C_β atoms, respectively, are observed on going from $CDCl_3$ to CF_3COOH, which is related to the protonation of *meso*-nitrogen atoms. In the ^{13}C NMR spectra of MPA^t in deuteriochloroform, the positions of the signals for the *tert*-butyl groups remain unchanged, and the signals for the $C_{\alpha'}$ and C_α atoms shift somewhat, depending on the nature of the metal atom.

Table 3. Chemical shifts (δ) of ^{13}C nuclei in H_2PA^t

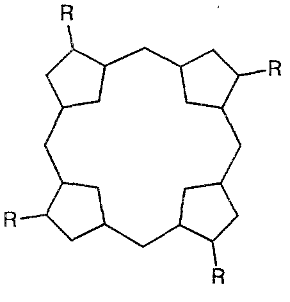


Carbon atoms	Solvent	
	$CDCl_3$	CF_3COOH
β′	158.8	159.4
β	128.7	126.1
α′	154.6	151.7
α	152.8	150.8
C	35.0	36.8
Me	32.2	31.4

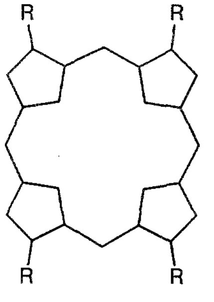
Identification of position isomers

Since the methods for synthesis of PA are mainly based on tetramerization of the starting porphyrinogens, resulting in the formation of a mixture (often random) of isomers as regards the positions of substituents in the macroring (randomers), the identification of positional isomers is one of the important problems of the structural chemistry of PA.

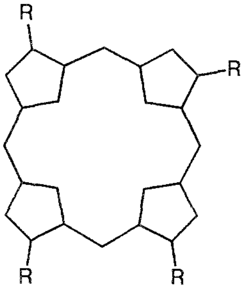
Individual randomers in the PA series have been completely separated and identified for the first time for H_2PA^t by high-performance liquid chromatography (HPLC). Of the four theoretically possible isomers, which can be attributed to I—IV types according to the nomenclature accepted for porphyrins,[55] only three isomers with identical EAS were registered.[60] The comparison of retention coefficients of individual fractions and analysis of their ^1H NMR spectra allow one to assign them to type I, III, and IV randomers in a ratio of 12 : 5 : 3.



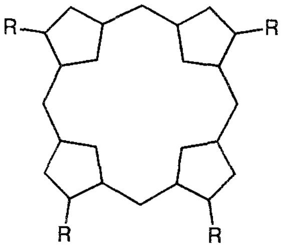
I



II



III



IV

It is shown that the ratio of the randomers formed is related to a great extent to steric factors. The II type randomer is not formed likely due to great steric hindrances.

Some differences are observed in fine-structure fluorescence spectra of individual randomers of H_2PA^t in a 5 : 5 : 2 light petroleum—diethyl ether—isopropyl alcohol vitrifying mixture at 4.2 K.[61] Different mutual arrangements of *tert*-butyl groups affect the vibrations at 500—650 cm^{-1} in which they participate and which can serve for the identification of randomers. For type I, III, and IV randomers, the most intense quasi-lines in the region of 710—740 cm^{-1} correspond to the vibrations involving $C_\alpha N_\mu C_\alpha$ fragments (at 739, 735, and 738 cm^{-1}, respectively). Bending vibrations of pyrrole moieties of all H_2PA^t randomers are observed at 717 cm^{-1}, however, their intensities differ.

Using a method of "hole-burning" in the contour of the long-wave absorption band of three individual H_2PA^t randomers in a 5 : 5 : 2 light petroleum—diethyl ether—isopropyl alcohol mixture at 4.2 K by monochromatic laser radiation with the wavelength of 618 nm, it has been shown[61] that the rate of the N—H-rearrangement of randomer I is lower than those of randomers III and IV. Thus, the randomer structure can serve as a criterion for selecting a compound of choice for the creation of carriers of frequency-selective optical information.

The fragmentation of H_2PA^t and several its metal complexes in electron-impact mass spectra has been studied. Similarly to porphyrins,[62] H_2PA^t give abundant peaks of the molecular ion $[M]^+$, which are supplemented by several isotopic peaks for metal complexes. Unlike spectra of porphyrins, the spectra of PA^t contain abundant peaks $[M-1]^+$, $[M-2]^+$, and $[M-3]^+$, and intensities of some of them are even higher than those of the $[M]^+$ peaks.[17] For example, for Co^{II} and Pd^{II} complexes the intensity of the $[M-1]^+$ peak is twofold and fourfold higher, respectively, than that of the $[M]^+$ peak, while the $[M-3]^+$ peak is the most abundant for the Cu^{II} complex. Low-intense $[M]^{++}$ ions are also observed in the mass spectra of complexes, which is consistent with the data for porphyrins.[62] The peaks corresponding to sequential dealkylation of the molecule are also observed, but there are no peaks for a completely dealkylated molecule, *i.e.*, $[M-4Bu^t]^+$. The most intense $[M-1-Me]^+$ peaks are observed for $PdPA^t$ and $CoPA^t$, and the $[M-3-Me]^+$ peak is observed for $CuPA^t$.

The mass-spectroscopic study of individual H_2PA^t randomers reveals some differences in their behavior, testifying that their structures have different ordering. The fragmentation in the mass spectra of some functionally substituted PA^t has also been studied. For example, peaks of molecular ions are the most abundant in the spectra of nitro-substituted PA^t. The peaks of fragments due to loss of alkyl and nitro groups are also observed.[38]

The $[M]^+$ peak of medium intensity with *m/z* 1300 (19 %) is observed at the inlet temperature of 500—570 °C in the electron-impact mass spectrum of the bridged dimer *p*-$H_2PA^tOC_6H_4C(Me)_2C_6H_4OH_2PA^t$-*p*. Weak peaks corresponding to the cleavage of methyl and *tert*-butyl groups from the $[M]^+$ ion are also observed. The peak of the ion with *m/z* 762 (100 %) corresponding to the elimination of H_2PA^t from the $[M]^+$ ion is the most abundant. The peak of an ion with *m/z* 538 (72 %) corresponds to $[H_2PA^t]^+$, and the peaks of ions with *m/z* 523 (51 %), 482 (14.5 %), and 368 (77 %) are caused by sequential cleavage of the methyl and one or three *tert*-butyl groups, respectively, from the latter.

X-ray electronic spectra (XES) of H_2PA^t and its several metal complexes have been studied by monochromatized Al-Kα radiation with the energy of 1486.6 eV (Table 4).[63] As in the case of PcH_2, XES of H_2PA^t exhibit a broadened line of N_{1s}, whose graphical resolution results in separation of two components corresponding to two types of nitrogen atoms with energies of 398.8 and 400.4 eV and half widths of 2.7 eV. The former corresponds to the aza-units of the molecule, and the latter is attributed to the pyrrole-type nitrogen atoms, whose energies almost coincide with those for PcH_2 and are somewhat shifted to the high-energy region compared to metal-free tetraphenylporphyrin. The ratio of their intensities is close to 3, which corresponds to the conventional structure with two hydrogen atoms at internal nitrogen atoms. XES of H_2PA^t randomers are identical.

On going from H_2PA^t to MPA^t, the band of N_{1s} is transformed into the narrow singlet with energies in the range of 398.7 to 399.5 eV and δ = 1.5 to 1.8 eV, which, by analogy with PcM, are assigned to the aza-type nitrogen atoms. The energy values of N_{1s} can be a criterion of the stability of the complex, and according to this criterion the stability varies in the series $Pb^{II} < Zn^{II} < Co^{II} < Ni^{II} < Pd^{II} < Cu^{II}$.

XES of octaethyl-H_2PA have been also studied.[7] The E_{N1s} values equal to 399.95 and 398.1 eV for protonated and nonprotonated isoindole nitrogen atoms and 398.75 eV for *meso*-nitrogen atoms were obtained. The values of the first two energies are higher by approximately 0.3 eV than that for octaethyl-H_2P, which agrees with the data of the quantum-chemical *ab initio* (SCF/DZ) calculation of the values of orbital energies of central nitrogen atoms. The same method showed that the introduction of peripheral substituents exerts an extremely strong effect on the value of the potential in the center of the PA macroring. For example, four nitro groups increase E_{N1s} of central nitrogen atoms by ~2 eV, four trifluoromethyl groups increase it by 1.3 eV, while perchlorination and perfluorination increase E_{N1s} by 1.35 and 1.7 eV, respectively. Eight cyano groups exert the strongest (2.6 eV) shift.

Table 4. X-ray electronic spectra of MPA^t*

M	E_{N1s}	δ_N	E_M	δ_M	$\Sigma E_M/\Sigma E_N$
			/eV		
H_2	400.4 398.8	2.7			
Cu^{II}	399.5	1.7			
Co^{II}	398.9	1.8	796.2, 780.2	3.3	0.11
Ni^{II}	399.2	1.5	873.0, 855.5	1.5	0.12
Pd^{II}	399.3	1.7	344.1, 348.9	1.5	0.125
Zn^{II}	398.7	1.7	1021.7	2.3	0.2
Pb^{II}	398.8	1.6	143.5	1.6	0.11

Note. E_{N1s} and E_M are the bond energies of 1s-electrons of nitrogen atoms and deep orbitals of metals, respectively; δ_N (δ_M) are the half-widths of bands of X-ray electronic spectra of nitrogen (metal) atoms, $\Sigma E_M/\Sigma E_N$ is the ratio of the surface areas of bands of X-ray electronic spectra of metal and nitrogen atoms.

* Experimentally measured and identified by T. M. Ivanova, senior researcher of State Research Institute on Organic Intermediates and Dyes.

Acid-base properties

In the conjugated system of the PA macroring, protons can theoretically add both to pyrrole (central) nitrogen atoms (by analogy with porphyrins) and *meso*-nitrogen atoms. The degree of protonation as well as the site and character of proton localization in the Pc macrocycle are the subject of numerous discussions.

First data on the behavior of PA and their complexes in acidic media were descriptive and did not concern the degree of protonation and spectral identification of individual protonated forms.[55] A more complete picture has been obtained in the study of protonation of H_2PA^t and some of its complexes by nitrobenzene solutions of aluminum bromide containing superacid $H[AlBr_4]$.[64] All four protonated forms were observed for CuPc in the 10^{-4}—10^{-1} mol L^{-1} concentration range of aluminum bromide, while in the case of $Cu^{II}PA^t$ only two first forms were present. This indicates a sharper drop of the basicity of the PA^t molecule upon its protonation. This is caused by lesser possibilities of delocalization of the positive charge in PA^t compared to that in Pc, because the electron density on *meso*-nitrogen atoms remains unchanged on going from H_2PA to H_2Pc.[41]

The study of acidic ionization of H_2PA^t by spectrophotometric titration in DMSO with a solution of tetramethylammonium hydroxide testifies that the ionization process occurs in two steps[65]:

$$H_2PA \overset{K_1}{\rightleftarrows} HPA^- + H^+;$$

$$HPA^- \overset{K_2}{\rightleftarrows} PA^{2-} + H^+ .$$

The addition of bases to a solution of H_2PA in DMSO results in reversible changes in EAS. An overall decrease in intensity of the bands of the initial neutral form is accompanied by the appearance of a new band at 528 nm. Two pairs of isobestic points at 561, 605 and 566, 606 nm, respectively, are observed. The differences in the symmetry of ionic forms of H_2PA also cause the differences in their EAS. The spectrum of the HPA^- form lowest in symmetry (C_{2v}) contains three bands, while that of the highly symmetric PA^{2-} form (D_{4h}) exhibits only one band.

The mobility of N—H protons is increased substantially by the introduction of electron-accepting nitro groups in H_2PA molecule. Dianionic forms of nitro-substituted H_2PA^t are formed in DMF or DMSO even in the absence of basic reagents.[38]

Redox properties

Redox properties of PA are of considerable interest from the viewpoint of utilization of PA as models of several biologically important compounds (heme, cytochromes, catalases, peroxidases, *etc.*) and for developing efficient catalysts based on these compounds for various processes.

The catalytic hydrogenation of H_2PA and their metal complexes, *viz.*, nonsubstituted tetramethyl-, octamethyl-, and tetracyclohexeno-derivatives of PA,[10–12,66] results in the formation of rather unstable compounds that decompose into the corresponding substituted succinimides. Hydrogenation of magnesium complexes can be controlled, when platinum black is used as a catalyst.[66] The absorption of two moles of hydrogen results in a 30-nm bathochromic shift of the long-wave band in the EAS accompanied by quenching of fluorescence. The resulting blue pigments are rapidly oxidized in air to form the original PA and small amount of unidentified colored compounds. The oxidation of octamethyl-H_2PA by chromic anhydride in sulfuric acid at room temperature gives[11] dimethylmaleimide in 80 % yield.

Redox transformations in the PA series can also be performed by photochemical reactions. For example, the photoreduction by hydrogen sulfide (or ascorbic acid) in the presence of potassium bromide results, judging from IR spectra, in the formation of the product of reduction of pyrrole units of the molecules.[55] Magnesium-tetramethyl- and -tetracyclohexeno-PA complexes in pyridine are photooxidized in daylight to form the corresponding imides.[11]

Electrochemical studies of PA are of great interest for elucidating the correlation between their structure and reactivity. Electrochemical reduction of PA was studied for the first time for magnesium-octaphenyl-PA (MgOPPA) in DMSO with tetrapropylammonium perchlorate as a supporting electrolyte and compared with analogous porphyrin complexes, in particular, *meso*-tetraphenylporphine (TPP).[67] Four one-electron waves are observed upon reduction of all compounds studied, and the reduction potentials for MgOPPA are considerably shifted to the anodic region compared to those of corresponding porphyrins. For example, $E_{1/2}$ of MgOPPA appear at −0.68, −1.11, −1.81, and −2.18 V, while those of ZnTPP are −1.32, −1.73, −2.45, and −2.67 V (relative to a saturated calomel electrode). The electrochemical reduction of octamethylthio-H_2PA and several its complexes in pyridine on a platinum electrode has been also studied.[68] One-electron reduction waves of the ligand at −0.396, −0.735, and −1.73 V are observed in the case of the metal-free compound. Magnesium, nickel(II), copper(II), and zinc complexes behave in a similar way. The only exception is the cobalt(II) complex, which forms the product of the reduction of the cobalt atom in $Co^{II}PA$ at the first stage ($E_{1/2}$ are equal to −0.385, −1.085, and −1.750 V). The electrooxidation of the latter also involves the central metal atom to yield a Co^{III} complex. The tendency to form Co^{I} and Co^{III} complexes upon electrochemical redox reactions was observed for cobalt porphyrins and CoPc as well.

When $Co^{II}PA^t$ is electrooxidized[63] in *o*-dichlorobenzene on an Au electrode, the potentiodynamic curve includes three anodic waves: the first two one-electron waves (1.15 and 1.25 V relative to AgCl/Ag) considerably overlap, while the third wave coincides with the beginning of oxidation of the supporting electrolyte. Since the values of potentials of the first two waves are close, only a two-electron oxidation product could be obtained in the individual form. Its EAS in *o*-dichlorobenzene (the Q band at 614 nm with the vibrational satellites at 593 and 560 nm) testifies that the radical cation of the Co^{III} complex is formed. The effects of the additions of coordinating bases on the redox potential values and the study of oxidation on an optically transparent electrode testify that the first electron is detached from the PA macroring.

The quantum-chemical calculation of a PA molecule by the self-consistent field method[7] shows that introduction of electron-accepting substituents into the PA macroring is an efficient method for increasing energies of the higher occupied MO of the macroring and, hence, the oxidation potential values. Four nitro groups increase the ionization potential of H_2PA from 6.53 eV to ~8.5 eV, and eight cyano groups increase it even to ~9 eV. Thus, this structural approach can be used for constructing stable catalysts of various oxidation processes in the series of PA derivatives.

Coordination chemistry

The coordination chemistry of PA is less covered in the literature than that of porphyrins and Pc. The similarity of their molecular structures allows one to find common regularities inherent in these macrocyclic systems.

Several works have been devoted to comparison of reactivities of PA and porphyrin ligands in complex formation with metal salts and protolytic stabilities of the complexes formed.[4] The study of the kinetics of formation of metal-PA complexes in the reactions of H_2PA with the corresponding metal acetates in pyridine shows that the reactions are first-order with respect to each reagent and correspond to the bimolecular mechanism previously established for the majority of porphyrins. Metals can be arranged in the series $Cu^{II} > Zn > Cd^{II} > Co^{II} > Mn^{II} > Ni^{II}$ on the basis of the rates of MPA formation. The reactivity of H_2PA is extremely high compared to porphyrins in reactions with transition metal salts, which is likely caused by the polarization of N—H bonds and stabilization of the ligand dianion due to aza-substitution.

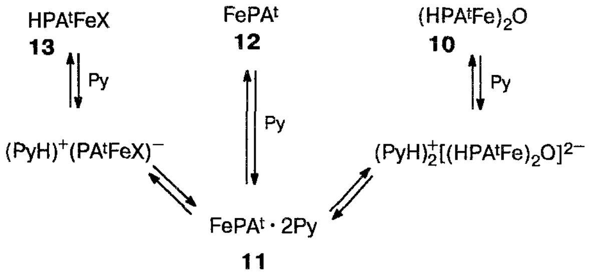
H_2PA is sufficiently stable in 100 % sulfuric acid at room temperature. The decomposition rate increases as the acid concentration decreases, which testifies in favor of the hydrolytic character of decomposition. MPA also undergo decomposition in aqueous solutions of sulfuric acid, which presumably occurs, as for MPc, in two steps: solvoprotolytic dissociation of protonated complexes to form a protonated free ligand followed by its decomposition. In aqueous sulfuric acid the decomposition of H_2PA and of the majority of complexes is first-order with respect to PA. According to kinetic stability, MPA form the following series: $Co^{II} > Pd^{II} > Ni^{II} > Cu^{II} > Zn$. MPA are considerably less stable than MPc. For example, even the most stable $Co^{II}PA$ dissociates tenfold faster in sulfuric acid than $Co^{II}Pc$. MgOPPA dissociates considerably faster than its nonsubstituted analog under comparable conditions, which can be accounted for destabilizing effect of phenyl substituents.

Several metal PA complexes tend to form axial adducts, *e.g.*, with molecules of nitrogen bases, alcohols, *etc.* For example, tetracoordinated iron(II)-octaethyl-PA (OEPA) with an intermediate spin ($S = 1$), according to the data of magnetic susceptibility, additionally coordinates axially two pyridine or 1-methylimidazole molecules to form diamagnetic bis-adducts.[69] The absence of an intermediate mono-adduct, as in the case of similar iron-porphyrin complexes, indicates that the equilibrium constant of binding the second ligand is considerably higher than that of the first one, which is explained by electron coupling in the low-lying t_{2g} orbital of the hexacoordinated complex. The values of equilibrium constants of $Fe^{II}OEPA$ are considerably greater (at least by two orders of magnitude) than those of iron(II)-porphyrin complexes. This is explained by a higher effective charge on the iron atom due to a stronger feedback of the iron atom with the macrocycle.

The formation of adducts of copper(II)-PA with organic bases in liquid and frozen solutions has been studied by ESR.[70] A decrease in the values of *g*-factors and increase in the HFC constants from the nitrogen atoms of pyrrole units compared to those of porphyrins are acounted for a decrease in sizes of the coordination cavity and shortening the Cu—N distance in $Cu^{II}PA$.

The coordination chemistry of iron-PA complexes, which are of special interest as models of heme-containing enzymes,[71] has been studied. The product of the reaction of H_2PA^t with iron dibromide was isolated as a μ-oxo dimer, $(HPA^tFe)_2O$ (**10**), with Fe^{II} as a central atom. Bis-pyridinate $FePA^t \cdot 2Py$ (**11**) was obtained upon treatment of μ-oxo dimer **10** with pyridine in benzene (Scheme 4). The vacuum sublimation of the latter results in removal of coordinated pyridine molecules to form $FePA^t$ (**12**), whose EAS testifies to its strong aggregation in solution. Acids (HX) transform dimer **10** into the "acidic" HPA^tFeX complex (**13**). The treatment with pyridine results in its initial transformation into pyridinium salt and then into dipyridinate **11**. EAS of μ-oxo dimer **10** in benzene contains a band at 596 nm ($\varepsilon = 6.5 \cdot 10^4$ L mol^{-1} cm^{-1}), while that of the HPA^tFeX complex exhibits bands at 550 nm ($\varepsilon = 1.8 \cdot 10^4$ L mol^{-1} cm^{-1}) and 662 nm ($\varepsilon = 1.9 \cdot 10^4$ L mol^{-1} cm^{-1}), which differs substantially from the spectra of "normal" PA, *e.g.*, $Cu^{II}PA^t$, and is in accord with the assumption about the unusual structure of the chelate unit. Only dipyridinate **11** has a spectrum close to spectra of usual PA.

Scheme 4



Despite the resemblance of coordination forms with $Fe^{II}Pc$, $Fe^{II}PA^t$ is distinguished by higher lability of pyridine molecules in dipyridinate and higher reactivity in the reaction with water that results in the formation of dimer **10**.

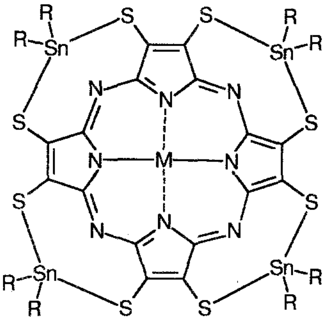
The electrochemical study of $Fe^{II}OEPA$ shows that the PA macrocycle stabilizes substantially the Fe^{II} state compared to the porphyrin ligand, which is explained by stronger π-accepting properties of PA.[69] Nevertheless, a Fe^{III} complex, $Fe^{III}ClOEPA$, has been isolated and investigated. The measurements of its magnetic susceptibility, ESR and Mössbauer spectra, and the XDA data point to its intermediate spin ($S = 3/2$), unlike high-spin $Fe^{III}ClOEPA$ ($S = 5/2$).

The synthesis of a paramagnetic dimeric μ-nitride PA complex, $[Fe(OPPA)]_2N$,[72] is described, and its properties are studied. The hyperfine splitting owing to the existence of a μ-nitride bridge is observed in its ESR spectra in nonpolar solvents at 77 K. The Mössbauer spectra indicate that Fe^{IV} predominates in $[Fe(OPPA)]_2N$. Its complex with pyridine reversibly binds oxygen to form a 1 : 1 adduct.

Rhodium-PA complexes demonstrate interesting transformations.[73] The reaction between H_2OEPA and $[Rh(CO)_2Cl]_2$ followed by treatment with iodine results in the formation of RhI(OEPA), whose sodium borohydride reduction product reacts with methyl iodine to give organometallic complex RhMe(OEPA). Irradiation of a benzene solution of the latter gives a $[Rh(OEPA)]_2$ dimer with the metal—metal bond. This dimer reacts, like $[Rh(OEP)]_2$, with MeI, MeNC, $(MeO)_3P$, and $CH_2{=}CH_2$ to form RhMe(OEPA) and RhI(OEPA), (OEPA)Rh(CN)(MeCN) and (OEPA)Rh(Me)(MeCN), and $(OEPA)RhPO(OMe)_2$ and $(OEPA)RhCH_2CH_2$—Rh(OEPA), respectively.

Special interest to the study of spectral, magnetic, and semiconducting properties of sandwich-type Pc and porphyrin complexes with rare-earth elements is observed in the recent time. A similar complex has been recently synthesized in the PA series as well: lutetium(III) bis[2,3,7,8,12,13,17,18-octa(*n*-octylthio)-5,10,15,20-PA], $Lu(OOTPA)_2$.[74] It was obtained in a high yield by the reaction of H_2OOTPA with lutetium acetate (2 : 1 molar ratio) in hexanol only as a paramagnetic "green" form. The structure of the free-radical nonprotonated form is assigned to this compound, like to the corresponding Pc complex, on the basis of ESR, NMR, and EA spectra. EAS of $Lu(OOTPA)_2$ differs substantially from the spectrum of the metal-free compound: in addition to the Q band (a peak at 670 nm with a shoulder at 652 nm and vibrational satellite at 628 nm in cyclohexane) and B band (a peak at 340 nm with a shoulder at 380 nm) it also contains a low-intense doublet at 427 and 473 nm and a band in the near IR range at 1150 nm caused by the presence of a free-radical, partially oxidized macroring in the molecule.

PA with a dual type of coordination of metal ions (with the central part of the molecule and with its outer sphere) were synthesized for the first time.[75] The dealkylation of the nickel(II)-octa(butylthio)-PA complex by treating it with sodium metal in a mixture of liquid ammonia and THF results in the formation of octasodium octamercapto-PA salt, which forms with, *e.g.*, bis(*tert*-butyl)tin dinitrate in aqueous methanol the following product:



R = Bu^t

EAS of the metal-free compound in dichloromethane contains a doublet of Q bands in the long-wave spectral region (716 and 648 nm), a band of lower intensity at ~508 nm, and the B band at 354 nm. Q bands of metal complexes appear as predominating bands with a vibrational satellite (for example, at 673 and 620 nm, respectively, for the copper(II) complex).

Polymeric porphyrazines

Taking into account that a comparatively recent review devoted mainly to the synthesis, properties, and practical application of polymeric PA (PPA) is available,[76] we will discuss here only briefly the most important specific features of these compounds. PPA are obtained by intermolecular condensation of tetracyanoethene (TCE) in the presence of metals or their derivatives (salts, acetylacetonates, *etc.*) in solvents or without them. For example, the reaction of copper(II) acetylacetonate with TCE *in vacuo* at temperatures from 160 to 300 °C results in the formation of CuPPA, a nonmelting black product insoluble in the majority of organic solvents and aqueous alkalis and acids, but soluble in DMF, pyridine, and concentrated sulfuric acid. A metal-free compound was obtained by the polymerization of TCE at 250 °C. These compounds are thermally stable and withstand heating to 500 °C for many hours. A parquet-type structure consisting of PA macrorings as its elements was assigned to these compounds mainly on the basis of the analysis of the IR spectra.

In the case of metal-PPA complexes, the initial formation of TCE complexes of radical-ion type $([(CN)_2C{=}C(CN)_2]^{-\cdot}M^+)$ is suggested, which further cyclize to form azaporphine structures.[77] The interaction of TCE with Ti^0, V^0, and Cr^0 bisarene complexes occurs in a similar way. These compounds are stable in the absence of oxygen or in the dark, while their irradiation in air is accompanied by the elimination of a metal from the macroring. As a rule, the activity and selectivity of polymeric PA complexes in catalytic redox reactions exceed those of their low-molecular analogs. Some PPA complexes, especially those containing copper and iron, demonstrate a high catalytic activity in the autooxidation of cumene.[76]

PPA can form micron-thick polymeric films on heating the activated metal surfaces in a TCE atmosphere at 150—400 °C for 5—20 h. They can serve, in particular, as stable protecting coverings. Electrophysical properties of such films depend on the temperature, time of heating, and procedure of film preparation. The maximum conductivity is observed for metal complexes with the maximum overlapping of their orbitals with the orbitals of the macrocyclic ligand.[78] The anisotropy of conductivity is observed for CuPPA films: σ in the direction parallel to the film surface is by 3—7 orders of magnitude higher than that in the perpendicular direction.

Aspects of practical application

Although the literature points to the possible use of PA as dyes and pigments,[1,2] they did not find wide practical application due to poor accessibility. However, the application of PA as "functional" dyes (FD) seems rather promising. This presently common name integrates dyes of various classes and compounds of similar structures that are used in technological fields that are nontraditional for them: radioelectronics, laser technique, microelectronics, systems of recording, storage, and displaying information, *etc.* The progress in this scientific and technological field is illustrated, in particular, in the Proceedings of the I and II International Symposia on Chemistry of FD (1989 and 1992, Japan).[79]

Phthalocyanines and their structural analogs, in particular, PA, are one of the most interesting and promising FD. Recent synthetic studies made it possible to establish regularities of the effect of structures of these compounds on their properties and have made several representatives of this class accessible, which possess a set of properties necessary for their practical use as FD. They involve high solubility in various organic and inorganic solvents, intense absorption in visible and near-IR spectral regions, high stability toward oxidation, ability to form ordered supramolecular structures, *e.g.*, Langmuir layers, a semiconducting character of conductivity, the existence as stable free radicals, *etc.*

Some applications of FD are based on spectral properties of their solutions: the selective absorption of dyes in certain spectral ranges. For example, PA can be used as additives for photostable light filters absorbing in visible and near-IR spectral regions. A composition based on H_2PA^t and MPA^t in poly(methyl methacrylate) was created for a polymeric light filter with absorption in the 560—620 nm region.[80] Ethanolic solutions of MPA^t ($M = Cu^{II}$, Mg, and Pd^{II}) were also used as bleachable light filters for tuning lasers based on rhodamine dyes.[81]

Optical storage devices based on the effect of selective laser "hole-burning" in nonuniformly broadened absorption bands of dye molecules have being developed in the recent time. For example, burning out holes in EAS of solid solutions of H_2PA^t in polystyrene has been studied, which made it possible to develop an information carrier with superhigh capacity.[82,83] Information is recorded in a picosecond time scale with a readout rate of 10^2—10^3 bit s^{-1}. $MgPA^t$ and (*p*-octylphenoxy)-H_2PA^t were also studied for these purposes. Tetranitro-PA^t and zinc-trinitro-PA^t complex were used as sensitizers of the photothermoplastic film based on poly-*N*-vinylcarbazole and styrene—butadiene copolymer for recording information by the beam of a helium-neon laser.[63]

Some applications of PA are based on the use of collective interactions of dye molecules, on their properties in the solid state. For example, 2,3,7,8,12,13,17,18-octaalkylthio-PA can form discotic-type liquid-crystalline mesophase, *e.g.*, the temperature interval of the existence of this phase for the corresponding copper(II) complex is 67.6—151.7 °C.[84] A set of H_2PA and their zinc and vanadyl complexes with electron-accepting nitro and cyano groups have been studied as spectral sensitizers for electrophotographic materials based on photoconducting polymers in the 550—635 nm region such as poly-*N*-vinyl-, poly-*N*-epoxypropylcarbazole, *etc.*[63] These compounds are highly selective to monochromatic radiation, and their sensitivity exceeds that of many other materials. Electrophotographic materials based on PA are promising for their use in systems of laser probing of the atmosphere (using the resonance absorption of sodium D line), laser microanalysis of admixtures, *etc.*

Finally, PA can be used owing to specific features of their molecular structures, for example, the existence of the chelate unit or coordinated metal ion. Octakis(4-sulfophenyl)-H_2PA is suggested as a reagent for quantitative determination of magnesium ions in aqueous solutions.[85]

The enhanced stability of PA derivatives toward the action of oxidants compared to Pc and porphyrins brings them into the class of very promising catalysts of various oxidation processes. The studies in this direction have just begun, but the results already obtained allow one to expect the creation of efficient and stable catalysts within this class of compounds. For example, the introduction of 10^{-4}—10^{-5} mol L^{-1} of $Co^{II}PA^t$ increases the reaction rate and the selectivity of styrene transformation in the liquid-phase oxidation of styrene by molecular oxygen in chlorobenzene at 120 °C.[86] The epoxidation is realized by activated oxygen due to the formation of its complex with the catalyst. $Mn^{III}PA$ complexes are also efficient catalysts of olefin epoxidation by peracetic acid under mild conditions.[87]

The search for efficient catalysts of hydroxylation of saturated hydrocarbons, which model the functions of cytochrome P-450, is very promising. In this respect PA turned out to be more suitable objects than porphyrins and even Pc.[71,88] For example, the oxidation of cyclohexane by cumene hydroperoxide (CHP) in the presence of $Co^{II}PA^t$ and $Fe^{II}PA^t$ under mild conditions (benzene, 20 °C, inert atmosphere) gives a mixture of cyclohexanol and cyclohexanone in a (1.2 to 1.5) : 1 ratio in an overall yield of 60 %. A mixture of 2- and 3-hexanols and 2- and 3-hexanones in an overall yield of 60 % was obtained from *n*-hexane in a similar way. $RO^{\cdot}$ and $RO_2^{\cdot}$ radicals are the reactive particles in this reaction. The number of moles of the oxidized substrate per mole of a catalyst in the presence of $Co^{II}PA^t$ reaches 1200, and in the presence of $Fe^{II}PA^t$ it is 3550. PA with electron-accepting substituents (nitro, cyano, and *o*-trifluoromethylphenyl-substituted PA) have been also studied as catalysts.[63] In the case of tetracyanotetrakis(*o*-trifluoromethylphenyl)-$Co^{II}PA$, the yield of cyclohexanol and cyclohexanone was 74 % and the catalyst is completely retained, while $Co^{II}Pc^t$ completely decomposed under analogous conditions. $ZnPA^t$ is an efficient sensitizer for the photochemical oxidation of 1,5-dihydroxynaphthalene by air oxygen to form 5-hydroxy-1,4-naphthoquinone (juglone), the known preservative for food industry.[63]

$Co^{II}PA^t$ on alumina has been used[63] as a catalyst for neutralization of nitrogen oxides under the action of ammonia to form molecular nitrogen (the degree of conversion was 99 %). A publication appeared concerning the use of $Co^{II}PA^t$ as a catalyst of chain transfer onto a monomer in the preparation of oligomeric alkyl methacrylates.[63] Co^{II} complexes with PA^t and tetranitro-PA^t very efficiently stabilize hydrocarbon oils toward high-temperature oxidative decomposition, which is an important problem in purification, storage, and exploitation of petrochemical products.[89]

Thus, PA derivatives are a class of compounds, which are an interesting from the theoretical viewpoint and promising for practical use and whose studies are at the initial stage as yet.

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