

PORPHYRINS.

36.* *cis,trans*-ISOMERISM AND ATROPISOMERISM IN MOLECULES OF ETHYLENEBISPORPHYRINS

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The synthesis of octaalkyl esters of 1,2-(meso-coproporphyrin-I-yl)ethane has been carried out from the corresponding copper complexes of meso-hydroxymethyl- and the nickel complexes of meso-dimethylamino-methylporphyrins. Their conversion into the corresponding trans- and cis-ethylenebisporphyrins has been investigated. On boiling in AcOH or xylene, ethylenebisporphyrins form an equilibrium mixture of cis and trans isomers. The cis and trans isomers of 1,2-di(octaethylporphyrin-I-yl)ethylene and the octaethyl ester of 1,2-di(coproporphyrin-I-yl)ethylene have been isolated and their interconversions investigated. It was demonstrated by PMR that the cis isomers of ethylenebisporphyrins have a rigid structure in which there is no free rotation of the porphyrin rings. The presence of two atropisomers is also a characteristic of the cis isomer of the coproporphyrin-I derivative. The formation of metal complexes in combination with the preparation of complexes with additional ligands enables control of the conformation of ethanebisporphyrins in solution. A mechanism has been proposed for the oxidation of ethanebisporphyrins to trans-ethylenebisporphyrins in acetic and other lower aliphatic acids.

Various conformationally fixed bisporphyrins, bischlorins, and bisphthalocyanines are widely used as adequate model systems for studying energy transfer processes in photosynthesis and in the investigation of natural catalytic systems [4, 5]. The greatest interest is in models in which the planes of the macrocycles are fairly close to one another with a distance between the centers of the molecules of 3.5-10 Å, and the actual planes of the molecules are set at a certain angle, forming an object in space reminiscent of the shape of a "hut with a gable roof."

Ethanebisporphyrins occupy a special place in the investigation of dimeric porphyrins, since they possess a series of unique properties, mainly the ability to be oxidized spontaneously by the oxygen of the air in acetic and other aliphatic acids to the corresponding *trans*-ethylenebisporphyrins [2, 3, 6-13], and the latter are capable of being transformed into *cis* isomers on boiling in acetic acid, or heating in xylene or other high-boiling solvents [2]. Heating dimeric chlorins in AcOH in the presence of moisture also leads to oxidation of the chlorin macrocycle to porphyrin [13].

We have developed three main new modifications of the synthesis of ethanebisporphyrins including a) the dimerization of the copper complexes of *meso*-alkoxymethylporphyrins in trifluoroacetic acid [14, 15], b) dimerization of *meso*-dimethylaminomethylporphyrins and their metal complexes in methyl (or ethyl) iodide [16, 17], and c) thermal dimerization of the phosphonium salts of the *meso*-triphenylmethyl iodides of metal complexes of porphyrins by heating in dichloroethane [18]. The synthesis of similar compounds, which had previously been available with extreme difficulty [19, 20], has become fairly routine. This enabled a more detailed investigation of the oxidation of ethanedimers to ethylenedimers and a study of the conformational transformations of these compounds in solution.

The results collated in the present paper are of the investigations carried out by us on the chemical properties of ethanebisporphyrins and concern mainly the formation and properties of the ethanebisporphyrins.

*For part 35 see [1]; for preliminary communications see [2, 3].

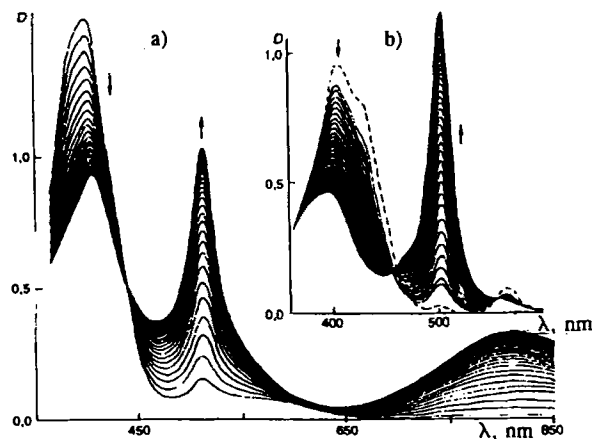
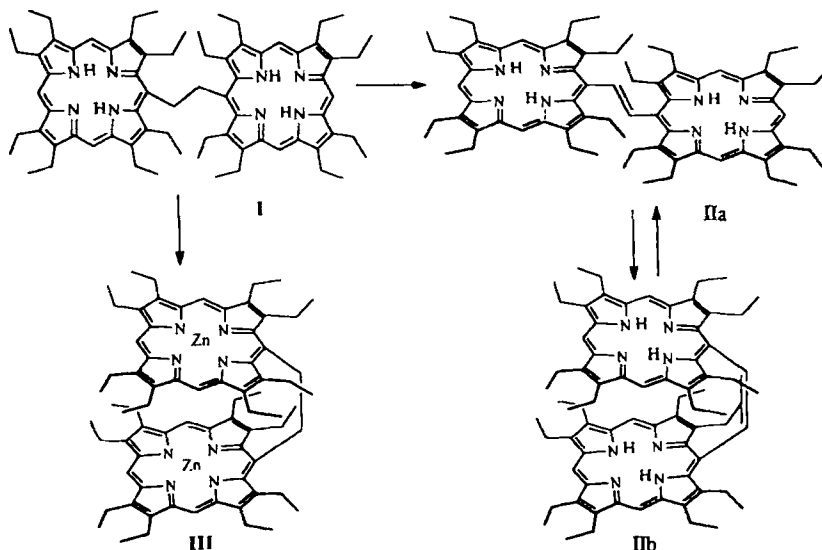


Fig. 1. Changes of the absorption spectra in the visible region on oxidation of (I) to (IIa): a) in EtCOOH, 30°C, 10 min intervals; b) in AcOH, 50°C, 5 min intervals; the dashed line is the spectrum immediately after solution at room temperature.

When investigating the physicochemical properties of ethanebisporphyrins (I), an unusual spontaneous oxidation was noted on maintaining it in AcOH at 60-70°C giving *trans*-ethylenebisoctaethylporphyrins (IIa) in 85% yield [6, 7] (Scheme 1).

Scheme 1



It was shown subsequently that the oxidation of ethanebisporphyrins to ethylenebisporphyrins proceeds readily in the lower aliphatic acids in quantitative yield even at room temperature in the presence of oxygen from the air. Some kinetic aspects of the mechanism of this conversion have been clarified [9].

The dynamics of the change of the electronic absorption spectra of the reaction mixture during the oxidation of the ethanedimer (I) in AcOH solution with time are shown in Fig. 1.

It follows from the spectral data that the oxidation process proceeds exceptionally directly. The presence of isobestic points indicates that only two products are present in the reaction mixture in detectable amounts in protonated form, viz. the initial ethane and the final ethylenebisporphyrins. The spectral characteristics of the dimers studied differ little from one another. Oxidation is inhibited significantly in stronger organic acids such as formic or trifluoroacetic (TFA). This indicates that the concentration of the monoprotonated form of the porphyrin is significant in solution for this process.

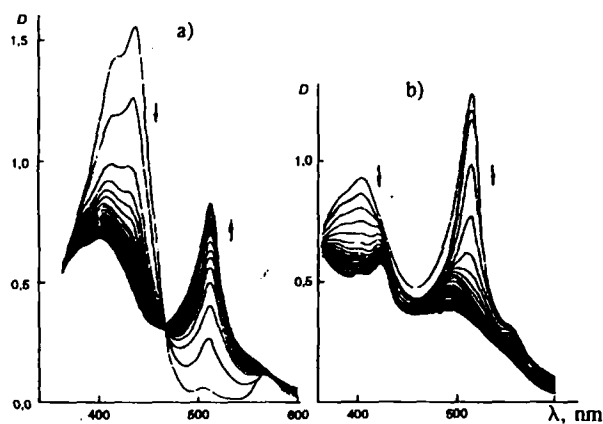
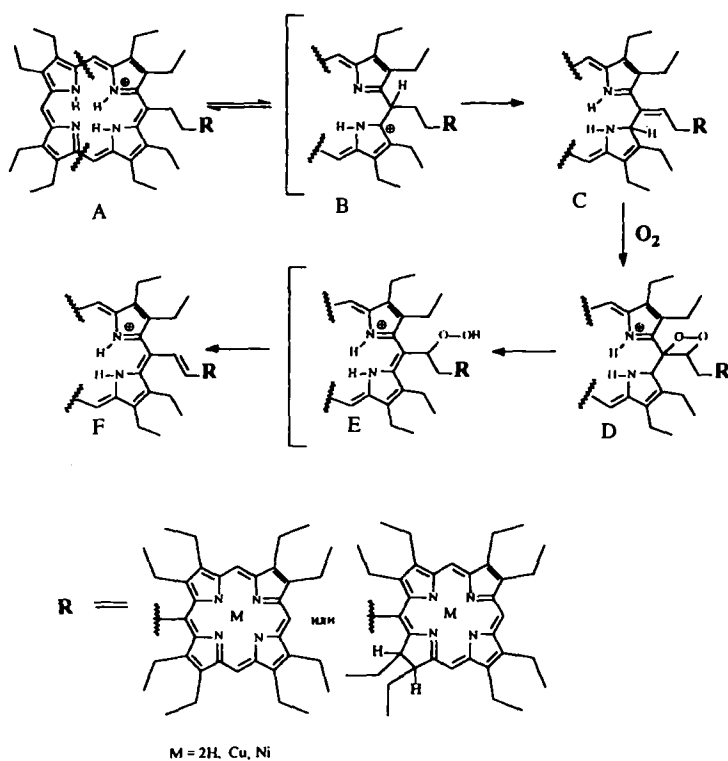


Fig. 2. Changes in the absorption spectra of a solution of dimer (I):
a) in EtCOOH at 30°C every 10 min in the absence of oxygen; b)
in EtCOOH at 30°C every 10 min on passing air into the cuvette.

The need for the participation of one or two monoprotonated porphyrin macrocycles in the conduct of the oxidation process remained unclear for a long time. We recently showed that monometal complexes of ethanebisporphyrins are also capable of being oxidized to the corresponding metal complexes of ethylenebisporphyrins, but at a higher temperature (for example, on boiling in AcOH) [21]. Since bismetal complexes of ethane dimers are not oxidized to the corresponding ethylenedimers, it follows that monoprotonation of only one of the porphyrin macrocycles is necessary to effect the oxidation. The oxidation mechanism proposed by us, which is based on an analysis of all the new experimental data available at the present time, as distinct from previously [9], is depicted in Scheme 2.

Scheme 2



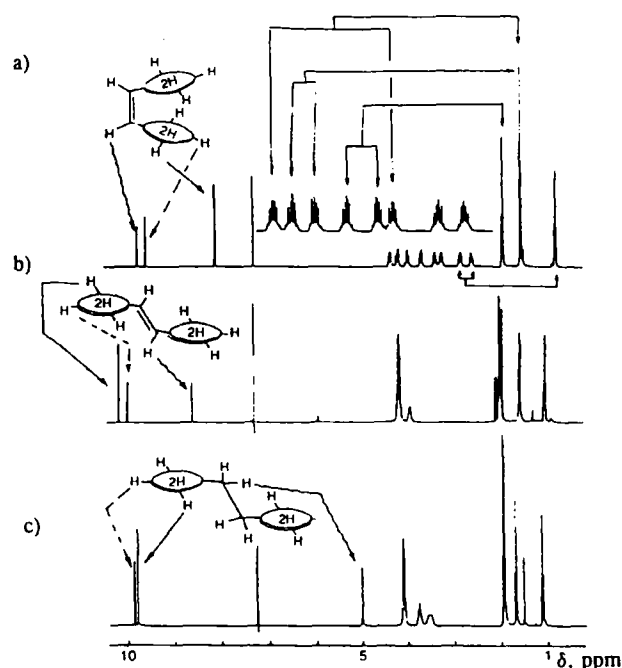


Fig. 3. PMR spectrum of dimers in CDCl_3 : a) (I); b) (IIa); c) (IIb).

The mechanism implies the formation in the first step of phlorin B from monocation A as a result of prototropic rearrangement. Compound B is isomerized into the reactive exoalkylidene C. The latter is readily oxidized by oxygen from the air dissolved in AcOH through the consecutive intermediates D and E into the *trans*-ethylene dimer F.

It is very remarkable that in the transformation of the ethanedimer into the ethylenedimer that the presence of oxygen in solution was absolutely unessential for the start of the reaction. Attempts by us to use specially deoxygenated aliphatic acids for studying this reaction were reflected very weakly in the kinetics of change of the spectral characteristics of solutions, which was indicated by the extremely similar electronic spectra of the intermediate still unoxidized product (probably exoalkylidene C) and the final ethylenedimer F (Fig. 2). Significant differences began to be displayed only after passing air through the reaction mixture. The greater the conversion of the initial ethanedimer into intermediate C, the lower was the yield of final ethylenedimer. In our opinion this may be explained as follows. Intermediate C is inclined to be transformed gradually into a large number of new products close to one another in structure, caused by migration of the positive charge through the whole macrocycle, which are oxidizable by oxygen not into the ethylenedimer but into a mixture of monomeric, dimeric, and possibly polymeric products difficult to analyze.

A characteristic feature of ethylenedimer (IIa) is its significantly higher chromatographic mobility on silica gel compared with the initial dimer (I) and also the unusual electronic spectrum in acid medium, with an intense absorption at 510 and a broad band at 770 nm (Fig. 1a). A detailed study of the photophysical and spectral properties of the *trans*-ethylene dimer (IIa) in the free base form in various solvents has been carried out recently by a group of Swedish and Belorussian investigators [22, 23]. They proposed the existence in solution of two conformational states P and U in a 5:1 ratio to explain certain new spectral characteristics of these compounds. Conformation P is a state in which the bridging double bond is directed perpendicular to the mutually parallel porphyrin macrocycles (in this case the porphyrins do not interact with one another through the bridging double bond). Conformation U is when the bridging double bond is located parallel to one of the macrocycles. In this, the zone of influence of the conjugation chain is extended, which leads to the appearance in the spectra of broad additional bands at 480-500 and 600-900 nm.

It follows from crystallographic data obtained by us [24] for the bisnickel complex of dimer (IIa) that an intermediate conformation between P and U exists in the crystalline state. The bridging double bond in it is turned by 72.5° relative to the two mutually parallel macrocycles, thereby providing minimal electronic interaction between the porphyrins.

The oxidation of ethanebisporphyrins (I) therefore leads selectively to the formation of the *trans*-dimer (IIa) under the given conditions (20-60°C, AcOH in the presence of air) (Fig. 3b).

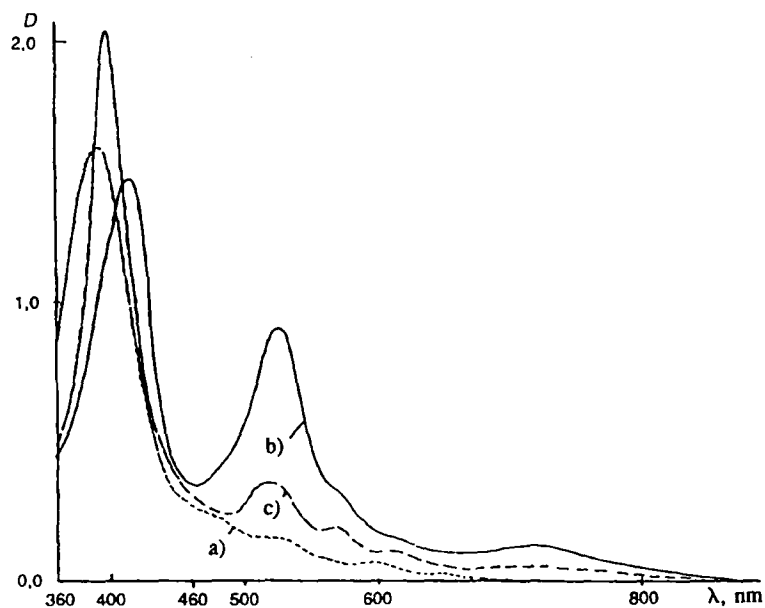


Fig. 4. Electronic spectrum of *cis* isomer (IIb): a) in toluene; b) in 0.1 % trifluoroacetic acid in toluene; c) in 5% trifluoroacetic acid in toluene.

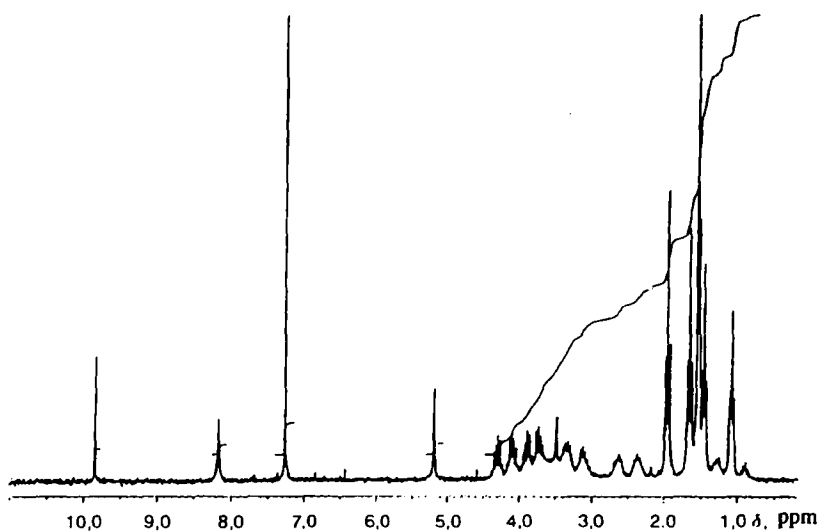


Fig. 5. PMR spectrum of dimer (III) in CDCl_3 .

However, on attempting to obtain dimer (IIa) from ethanebisporphyrins (I) in boiling AcOH we constantly observed a significant drop in the yield of the dimer (to 27-30%) and the emergence of a new polar product (IIb) (50-60% yield), the mobility of which on silica gel was comparable to the mobility of the ethanedimer (I).

The electronic spectrum of (IIb) (Fig. 4) differed significantly from the four-band spectra of known porphyrins since it contained only a broadened Soret band (391 nm) with a shoulder at 480 nm and three less informative bands in the visible region at 525, 595, and 645 nm. The spectra of the protonated forms also had their own special features. On gradually adding TFA, a displacement of the Soret band to 415 nm occurred first, then an intense peak appeared at 510-520 nm and also a very broad band at 720-760 nm.

Further addition of TFA led to a red shift of the Soret band to 398 nm and a four-band spectrum in the visible region (λ_{max} 519, 566, 609, and 708 nm). The intensities of all the bands in the spectrum, with the exception of the Soret band, were significantly reduced.

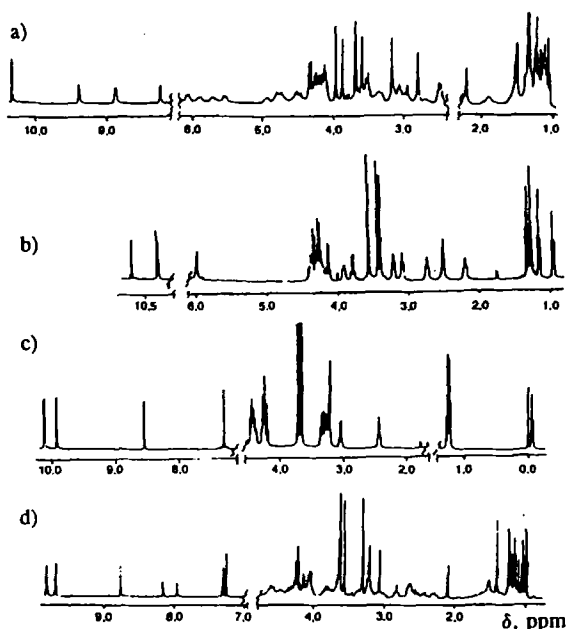


Fig. 6. PMR spectra of dimers in CDCl_3 : a) (IX); b) (IX) with added CF_3COOD ; c) (Xa); d) (XIIa).

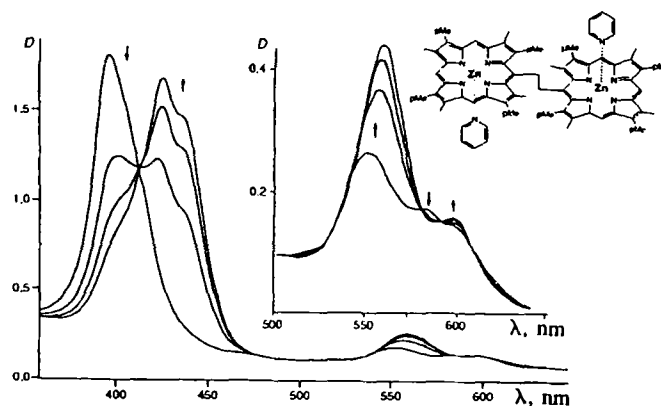


Fig. 7. Change in the electronic spectrum of dimer (XIX) on gradually adding pyridine (from 0 to 10%).

Analysis of the PMR spectrum of (IIb) showed the presence of signals for *meso* protons at low field and NH protons at high field, which unequivocally indicated the retention of the porphyrin macrocycle (Fig. 3c). In the *meso* proton signal region, three singlet signals were observed at 9.69, 9.50, and 8.03 ppm at a ratio of 1:1:2, among which were also found the signals for the bridging ethylenic protons. To identify the *meso* proton signals the dimer (Ia), deuterated only at the *meso* positions, was obtained from the initial ethanebisporphyrins (I) by treatment with 90% D_2SO_4 . The characteristic signals for the *meso* protons of dimer (I) at 9.87 and 9.82 ppm [8] were absent from its PMR spectrum. After boiling dimer (Ia) in acetic acid, the signals at 9.50 and 8.03 were absent from the spectrum of the product formed, but the signal at 9.69 ppm remained unchanged. From this it may be concluded unequivocally that (IIa) is a *meso* substituted porphyrin. However, it may also be concluded from the presence in its mass spectrum of an intense molecular ion peak with m/z 1092 that the isolated compound is also an ethylenebisporphyrin. The signal at lowest field (9.69 ppm) therefore corresponds to two protons of the ethylene bridge and the signal at 8.03 ppm to the protons at the 10,10' and 20,20' *meso* positions. The displacement of this signal by 2 ppm and of the two NH proton signals by almost 3 ppm (-4.84 and -5.67 ppm) towards high field compared with the *trans* isomer (IIa) (-2.72 ppm) as a result of the mutual shielding effect of the ring currents indicates a *cis* disposition of the porphyrin rings.

The signals of the *meso* protons in the 15,15' positions furthest removed from the neighboring macrocycles undergo the least displacement compared with dimer (IIa) (Fig 3b). The mutual influence of the porphyrin rings also shows up on the signals of the side ethyl substituents, which were displayed as a collection of 8 sextets (more precisely, a doublet of quartets) at 2.55-4.28 ppm for the methylene protons, since each CH₂ group is an AB system with $J = 15$ Hz interacting with the methyl group with $J = 7.5$ Hz [a complete assignment of the signals in the PMR spectrum of *cis* isomer (IIb) has been carried out by A. M. Shul'ga using the nuclear Overhauser effect (NOE)].

On protonation of isomer (IIb), a displacement towards low field of the signals of the bridge, 10,10', and 20,20' protons occurred. This is probably linked with the unfolding of the porphyrin macrocycles relative to one another in such a way that the angle between the planes passing through each of the four nitrogen atoms in the porphyrins must become significantly more than 1.9°C. This is the angle characteristic of the neutral molecule due to the mutual repulsion of the positively charged macrocycles. Such a conformation weakens the mutual shielding influence of the ring currents on the *meso* positions neighboring the ethylene bridge and also leads to a displacement of the signals of these protons of approximately 0.5 ppm towards low field.

The formation of the *cis* isomer (IIb) is linked totally with the increase in reaction temperature. In fact, if ethanebisporphyrin (I) is initially heated at 60°C in AcOH [6] to form the *trans* isomer (IIa) and then without isolating the product the solution is boiled thoroughly, a mixture of isomers (IIa) and (IIb) is formed in the same ratio (1:2) as in the previous experiment.

The interconversion of (IIa) and (IIb) with the formation of the thermodynamic mixture of isomers was observed by PMR spectroscopy on heating them in deuterated *meta*-xylene. In this case, significant interconversion of isomers began only at $T > 130^\circ\text{C}$. Thus, the reaction mixture after heating (IIa) at 140°C for 4 h consisted of 75% isomer (IIa) and 25% isomer (IIb). The ratio of isomers was unchanged after heating for 2 h further. It is possible that isomerization of the *trans*-ethylenebisporphyrins to the *cis* isomers occurs by initial activation of the U conformer.

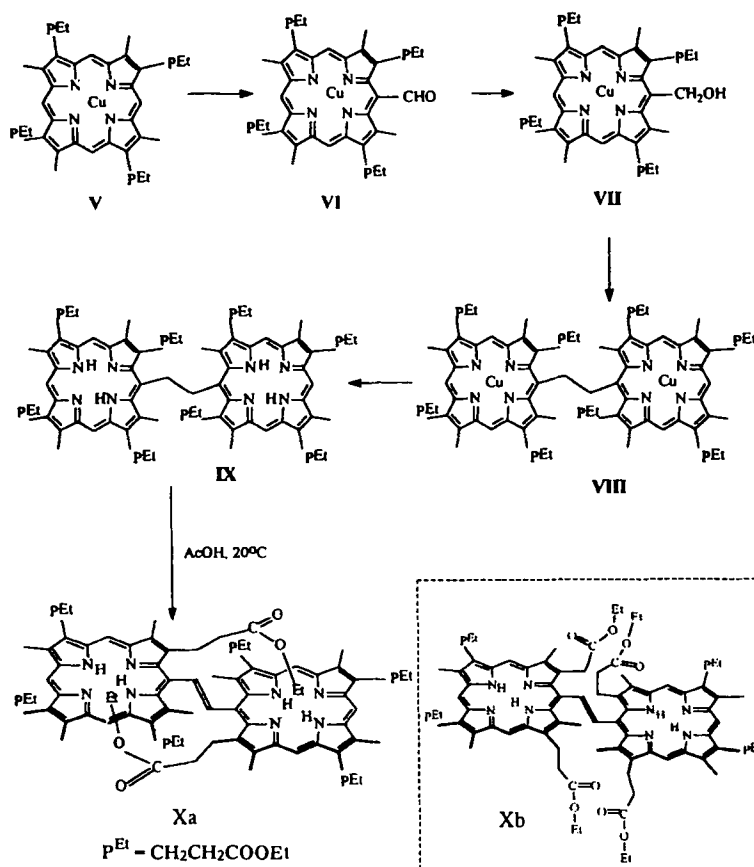
Interpretation of the PMR spectra of ethylenebisporphyrins (IIa) and (IIb) afford an explanation of the unusual chemical shift of the 10,20-*meso* protons of ethanebisporphyrin (I) (Fig. 3a) compared with mono-*meso* substituted porphyrins. In the latter these signals are usually found at higher field than the signal of the 15-*meso* proton (according to [25] the signals of the 10,20-*meso*-H and the 15-*meso*-H for *meso*-methyloctaethylporphyrin are displayed at 9.93 and 9.72 ppm). In CDCl₃ (Fig. 3a) the signal of 10,20-*meso*-H for dimer (I) is found at higher field than the signal of 15-*meso*-H. In deuterated xylene its position is displaced even further towards high field (to 9.02 ppm). If this chemical shift is compared with the chemical shifts of the same protons in *trans* (IIa) (10.15 ppm) and in *cis* isomers (IIb) (8.22 ppm in CDCl₃ and 7.86 ppm in CS₂) then it is evident that as a result of rotation around the single bridge bond there are in solution a set of cisoid (shielded) and transoid (restrained) conformations displayed as an averaged signal for the 10,20-*meso*-H in dimer (I). A reduction in temperature to 173 K (CS₂) led to a predominance of the restrained conformation and correspondingly to a displacement of this signal to low field (from 9.07 to 9.88 ppm) with a practically unchanged position for the signal of the 15-*meso*-H (9.72-9.73 ppm). In the transoid conformation (dihedral angle $C_{\text{meso}}-C=C-C_{\text{meso}}$ close to 180°) the mutual influence of the ring currents of each of the porphyrin macrocycles is practically absent and the PMR spectrum becomes similar to the spectra of the usual meso-alkylporphyrins. Protonation also leads to the generation of an elongated (drawn out) transoid conformation.

In the case of the ethanedimers it is readily possible to change the conformation using the specific ability of a series of metal complexes to form dimeric associates in solution. It was shown recently by PMR that the biszinc complex (III) of dimer (I) exists in chloroform as a stable cisoid conformer [26]. In its PMR spectrum (Fig. 5) the signals of the methylene protons of the ethyl substituents are also a set of eight sextets of signals analogous to the signals of the *cis* dimer (IIb), and the signals of the 10,20 *meso* protons are displaced to 8.18 ppm in high field [chemical shift of the 10,20 *meso* proton signals of (I) are 9.50 ppm], i.e., into the region characteristic of derivatives of the *cis*-ethylene dimer (IIb). The broadened singlet of the bridge protons (CH₂-CH₂) at 5.2 ppm had an insignificant low field displacement compared with the metal-free dimer (I) as the free base (5.00 ppm, CHCl₃), but was significantly different from the corresponding signal of the bisnickel complex of dimer (I). The precise position of the signal of the bridge protons in the latter was not established due to the overlap with the multiplet signals of the methylene protons of the ethyl substituents [19].

It is interesting that the biszinc complex of *cis*-ethylenedimer (IIb) which is readily soluble in chloroform is converted after several days into the corresponding difficultly soluble *trans* isomer which is precipitated from solution [27]. This fact indicates the advantage of the extended form for a rigid ethylenebisporphyrin. The process of isomerization of zinc complexes of *cis*-ethylenedimers into the *trans* isomer may be accelerated significantly by adding pyridine to the solution. Pyridine forms pentacoordinate complexes with the central zinc atom, which assists unfolding into the extended form [27].

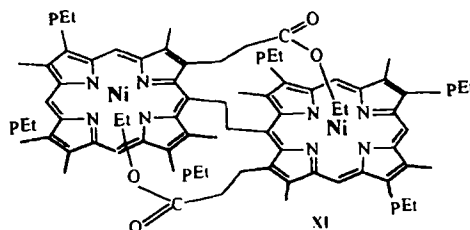
Due to steric hindrance in the *cis*-ethylenebisporphyrins there is no mutual rotation of the porphyrin macrocycles relative to the common bridge bond since, as follows from x-ray data obtained for the bis copper complex of (IIb) [10, 28], these two macrocycles are almost parallel. The angle between the two planes passing through the central nitrogen atoms in each porphyrin is 1.9° and the distance between them is 3.36 Å. Consequently, one is forced to conclude that in the case of unsymmetrical porphyrins on forming *cis* isomers (and possibly *trans*-ethylenedimers), stable atropisomers must also be formed. We have investigated this process when obtaining dimeric porphyrins starting from the tetraethyl ester of coproporphyrin-I (IV) (Scheme 3).

Scheme 3



The Cu complex of *meso*-hydroxymethylporphyrin (VII) was obtained from the Cu complex (V) of (IV) by Vilsmeier formylation to complex (VI) and reduction with NaBH_4 . The formation of dimer (VIII), its demetallation to bisporphyrin (IX), and conversion into the trans dimer (Xa) were effected by the procedures in [3]. The greatest difficulty when obtaining dimer (IX) with a high degree of purity was the stage of demetallating complex (VIII), since this process is accompanied by partial hydrolysis of ester groups on prolonged (up to 6 h) storage of complex (VIII) in conc. H_2SO_4 . The need for such extended treatment is caused by the fact that after removal of the first copper atom demetallation of the second occurred extremely slowly. Furthermore, to obtain high quality PMR spectra, the presence of even trace amounts of porphyrin copper complex is inadmissible.

Scheme 4



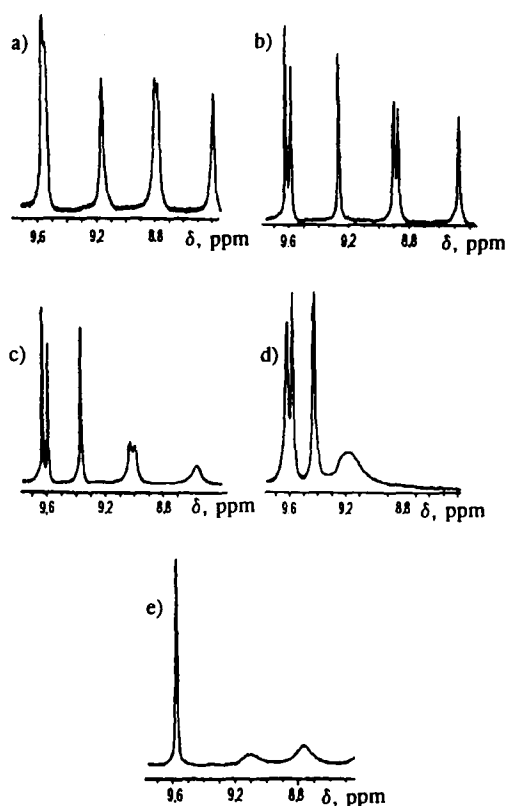
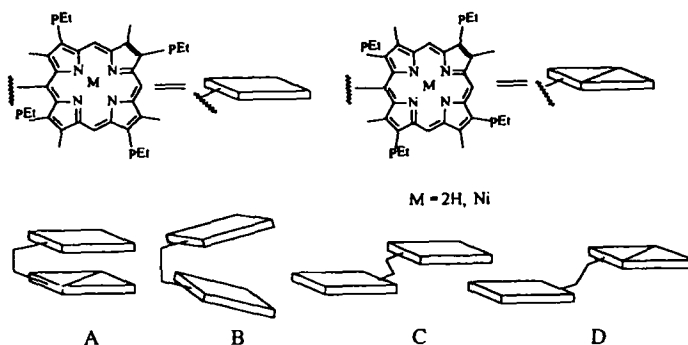


Fig. 8. PMR spectrum of dimer (XXIII) in CDCl_3 in the *meso* proton region at: a) 293 K; b) 273 K; c) 243 K; d) 218 K; e) 318 K.

It is most probable that dimer (VIII) and possibly dimer (IX) have in the crystalline state a molecular structure like the corresponding bisnickel complex (XI) obtained by us recently from the tetraethyl ester of the nickel complex of meso-dimethylaminomethylcoproporphyrin-I [29].

However, an approximately similar picture of five signals in the ratio 2:1:1:1:1 may be observed in the PMR spectra in CDCl_3 of both the Ni complex (XI) and the free base (IX) of the ethane dimers (Fig. 6). This fact was interpreted incorrectly by us as the possible presence in solution of four conformers of type A, B, C, and D (Scheme 5).

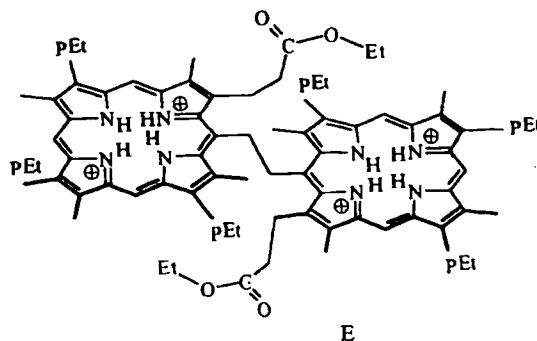
Scheme 5



For all these conformers the singlet at 9.85 ppm in the traditional region for *meso* protons corresponds absolutely to the protons in the 15,15' positions for which the atropisomerism may not cause significant structural or magnetic differences and the remaining four signals are the 10,10',20,20'-*meso* protons hypothetically of all the A, B, C, and D conformers. We

were unable to assign each of these four signals to any definite conformation. However, in the PMR spectrum of dimer (IX) in the protonated form (Fig. 6b), the signals from the 10,10',20,20'-*meso* protons appeared as two very close singlets at 10.28 and 10.27 ppm, which indicated the emergence of a single atropisomer E in the transoid conformation.

Scheme 6

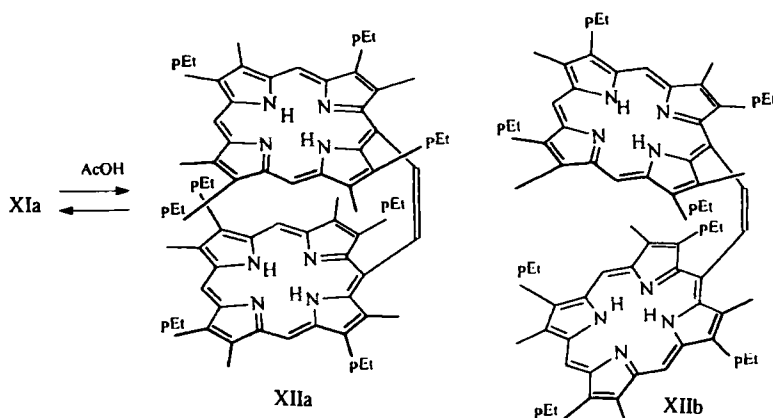


Oxidation of the ethanedimer (IX) occurs stereoselectively. On analysis of the PMR spectrum of ethylenedimer (Xa), not even trace amounts of the alternative dimer (Xb) were detected. The PMR spectrum of *trans*-dimer (Xa) in CDCl_3 indicates that this compound is in the form of a single atropisomer, which probably corresponds to structure (Xa). It is the most favorable from steric considerations since a very strong mutual overlap of the two oppositely located propionic acid ester residues must exist for structure (Xb). In our opinion, such stereoselectivity is connected with the steric features of the propionic acid ester residues located near to one another. A characteristic trait of this spectrum is the displacement (Fig. 6c) towards high field of the signals of the protons of the two propionic acid ester residues found together with the ethylene bridge. For example, all the $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ protons are displaced from 1 to 1.5 ppm in comparison with the usually observed signals for monomeric porphyrins. The mutual effect of the ring currents shows up particularly strongly on the two ethyl ester groups, the triplet methyl groups of which are at -0.07 ppm. This indicates that they are located above the planes of the porphyrin macrocycles near the center of the molecule. The mutual disposition of the propionic acid ester residues in the *trans* isomer (Xa) in solution practically completely coincides with the spatial distribution of these same substituents for the Ni complex of the ethanedimer (XI) in the crystalline state [29]. A similar picture is observed on comparing x-ray data for the transoid conformation of the bisnickel complexes of dimers (I) [30] and (IIa) [24].

Boiling *trans* isomer (Xa) in AcOH or in *o*-xylene leads to an equilibrium mixture of (Xa) and the *cis*-dimer (XII) in a ratio of 23:77 which indicates the favorability of the existence of the *cis* form. Probably on forming the *cis*-dimer, the long side-substituents interact with one another with the formation of a compact knot, which makes such a state thermodynamically more favorable.

It may be concluded unequivocally from the presence of double signals in the region of *meso* protons and bridge $\text{CH}=\text{CH}$ protons in the PMR spectrum of *cis*-dimer (XIIa) (Fig. 6d), which like the *cis*-dimer (IIb) are found at low field, that the conversion of the *trans* isomer into *cis* is accompanied by isomerization into two stable forms (XIIa) and (XIIb) in a ratio of 2:1. It is most probable that the sterically more favored structure (XIIa) is the atropisomer formed in a large amount.

Scheme 7



As is evident from Fig. 6d, the signals of the 10,20-*meso* protons of the atropisomer (XIIa) differ very strongly from one another (8.71 and 7.30 ppm) and from the signal of the 15-H-*meso* proton (9.60 ppm). This fact indicates that the atropisomer being considered has a canted (twist) conformation in which the torsion angle between $C_{meso}-C=C-C_{meso}$ is probably about 50-60°C. In this case, minimum overlap will be observed of the peripheral methyl groups on one ring and the ethoxycarbonyl ethyl substituents on the other, which are located one opposite the other. At this mutual disposition of the macrocycles, two *meso* protons (one from each porphyrin) will be found in a region of maximum effect of the ring currents from the neighboring porphyrin macrocycles and two others will be removed to a significant extent from the region of influence of the ring currents of the neighboring porphyrin. This leads to a displacement of the *meso* protons towards low field into the region of the signals of the 15,15'-*meso* protons. On the other hand, for atropisomer (XIIb) the signals for the 10,20-*meso* protons at 8.12 and 7.93 ppm occupy an intermediate position relative to the analogous signals for isomer (XIIa) but differ insignificantly from one another in chemical shift. This fact may only be explained in the following way. As a result of the mutual steric influence of the bulky ethoxycarbonyl ethyl substituents on each of the porphyrin rings located opposite one another, the dihedral angle between the planes constructed through the four pyrrole nitrogen atoms of each of the porphyrins is significantly greater than in the case of the twist-isomer (XIIa). This leads to a reduction in the averaging of the mutual effect of the ring currents on the 10,20-*meso* protons.

Comparison of the PMR spectra of the *cis*-dimers (XIIa,b) and the ethanedimer (IX) in the *meso* proton region (Fig. 6a and 6d) enabled a fairly validly drawn conclusion. The presence in chloroform solution of only the two shielded A and B and not all the four possible conformational states is a characteristic of the ethanedimer (IX). In their spatial parameters, A and B are close to the atropisomers of (XIIa) and (XIIb).

The presence of the atropisomeric conformations in (IX) was also confirmed by the fact that in its spectrum (Fig. 6a) four groups of signals were observed for the bridge CH_2CH_2 protons. These were two doublets and two complex multiplets which interact among themselves in pairs. The doublets (5.55 and 4.96 ppm, $J = 9.7$ Hz) correspond absolutely with the symmetrical conformation (XIIa). An increase of temperature increases the rate of interconversion of the various forms. At 140°C the spectrum of dimer (IX) is close to the spectrum of dimer (I) in the region of the bridge and *meso* protons, i.e., the conformational differences disappeared.

The data obtained explain the significant difference in chemical shift of the signals of the *meso* protons in dimer (IX) compared with dimer (I) [8]. In the spectrum of dimer (I) there is a signal for the 10,10',20,20'-*meso* protons located closed to the signal of the 15,15'-protons. This fact indicates that the main state for the given isomer in solution, the transoid restricted conformation, is close in geometrical parameters to the *trans*-dimer (IIa).

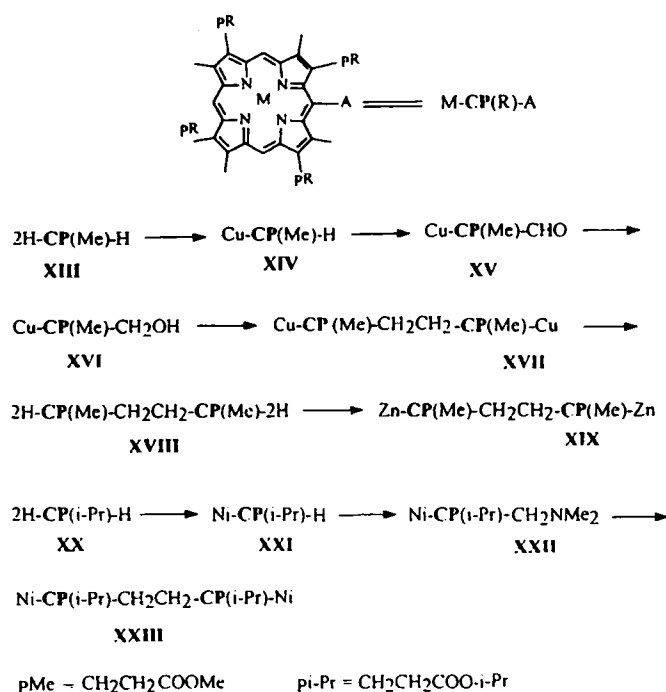
The following main conclusions may be drawn based on the factors given.

1. The conformation of the ethanedimers in solution depends to a significant extent on the composition and mutual disposition of the peripheral β -substituents.
2. Protonation of the porphyrins assists mutual unfolding of the macrocycles and the generation of a transoid conformation.
3. The formation of metal complexes may significantly influence the conformational state of ethanebisporphyrins (for example, the zinc complex of dimer (I) in chloroform is found exclusively in the cisoid shielded conformation and the nickel complex of the same dimer is found in the transoid).

We obtained the biszinc complex (XIX) to clarify the possibility of the directed control of the conformational state of ethanebisporphyrins by introducing metals capable of forming complexes with extra ligands. Starting from the tetramethyl ester of coproporphyrin-I (XIII) by formylation of its Cu complex (XIV) to the formylporphyrin (XV) with subsequent reduction to the *meso*-hydroxymethyl derivative (XVI), dimerization of the latter in TFA to the complex (XVII), and demetallation in conc. H_2SO_4 gave dimer (XVIII). We hoped that the zinc complex (XIX) of this dimer, by analogy with the known complex (III), will exist in chloroform also in the cisoid form. Starting from this premise, we assumed that addition of pyridine to a solution of complex (XIX) would lead to the formation of the transoid conformation as one or two atropisomers.

Dimer (XVIII), like the octaethyl ester (IX), had similar signals for the *meso* protons in the PMR spectrum, which indicates the identity of the conformational states of these compounds in solution. Principal differences were observed only in the region of NH protons. Four fairly narrow signals equal in intensity were detected in the spectrum of dimer (XVIII), which in our view indicated even more the existence of two conformers in equal concentration.

Scheme 8



Complex (XIX) in chloroform is in fact found as cisoid atropisomers. This may be judged from analysis of the electronic spectra in which were observed an appreciable hypsochromic shift of the Soret band (to 395 nm), which is characteristic of sandwich dimeric associates. A concentration dependence of dimer content in solution always exists for associates of monomeric porphyrins, but in the case of complex (XIX) dilution of solutions had no effect on the spectral characteristics. However, on adding pyridine conversion of the dimer into a more elongated transoid form was noted together with coordination of the central zinc atoms with pyridine. The transoid form is displayed in the electronic spectrum as the emergence of new peaks at 423 and 432 nm. The process of titrating complex (XIX) with pyridine is shown in Fig. 7. The presence of an isosbestic point indicates the equilibrium character of the process. In the visible region the unusual spectrum having a broadened absorption band at 560 and two shoulders at 583 and 596 nm is converted on adding pyridine into a traditional two-band spectrum with maxima at 559 and 597 nm, characteristic of zinc complexes in the presence of pyridine. Such a spectrum indicates the absence of electronic interactions between the macrocycles.

However, we failed to obtain a graphic picture of the simultaneous presence in solution of cisoid and transoid forms with the aid of PMR spectra. Gradual addition of pyridine to a solution of a sample in deuterochloroform led only to a strong broadening of all signals and poorly informative spectra were obtained. Only in pure deuteropyridine was a high-grade PMR spectrum obtained. From the presence of only three singlets of *meso* protons, it follows that dimer (XIX) is in a single transoid atropisomeric form. This differs from dimer (XI) in the crystalline form only in the fact that the methoxycarbonylethyl substituents neighboring the *meso* bridge are not located near the centers of the opposite macrocycles.

To elucidate the effect of solution temperature on the conformational state of ethanedimers, the nickel complex (XXIII) was synthesized by the method used by us for the synthesis of dimer (XI) [29]. The tetraisopropyl ester of coproporphyrin-I (XX) was formylated according to Vilsmeier giving complex (XXI), reduction of the intermediate imino salt gave complex (XXII), and dimerization of the latter in MeI gave dimer (XXIII) in 45-55% overall yield. Choice of the tetraisopropyl ester of coproporphyrin-I was based on the hypothesis that the signals of the isopropyl groups might be more correctly attributed in the PMR spectra since they would not be masked by the multiplet signals of the $\text{CH}_2\text{CH}_2\text{CO}$ groups in the event of the simultaneous existence in solution of several *atrop* isomeric conformations.

On increasing the solution temperature to 318 K (Fig. 8e), a marked broadening of the signals of the 10,10' and 20,20' *meso* protons occurred. An increase in the rate of interconversion of transoid and cisoid conformations was not reflected in the chemical shifts of the 15,15' proton signals, which were converted into a narrow singlet.

We assumed that a reduction in solution temperature might lead to the creation of more favorable conditions for the emergence of transoid conformations in solution, as, for example, in the case of dimer (I), which precedes the initial stage of

crystallization. It is known that in the crystal unit cell the bisnickel complexes of ethanedimers are found exclusively in the form of a single transoid atropisomer [29, 30].

Successive reduction of temperature (Fig. 8, a-d) leads to a broadening of the signals of the 10,10', 20,20' *meso* protons located at higher field. Only the signal of one of the 10,10', 20,20' *meso* protons at low field did not change its shape and was only displaced downfield towards the signal of the 15,15' *meso* protons. The displacement of the three high field signals with the formation of one broadened signal at 218 K (Fig. 8, d) suggests the existence of dimer (XXIII) at this temperature predominantly in a transoid conformation [see PMR spectrum of the zinc complex of (XIX) in pyridine].

The *cis-trans* isomerism detected by us has enabled numerous problems of the spatial organization of dimeric porphyrins to be solved. The data obtained on the possibility of isomerization of not only the free bases of ethylenebisporphyrins but also their monometal complexes [21] broaden significantly the prospects of using similar compounds for studying photophysical, catalytic, and other properties of tetrapyrrole compounds. The use of metal complexes, the formation of complexes with extra ligands or protonation, and also possibly long-chain peripheral β substituents on the porphyrin rings are several ways of obtaining spatially rigid ethanebisporphyrins.

EXPERIMENTAL

The PMR spectra were taken on Bruker WM 360 and Varian UNITY 300 instruments in CDCl_3 . The internal standard was TMS or the CHCl_3 signal at 7.25 ppm. Electronic spectra were taken on Hitachi 320 and Varian Carey 3 spectrophotometers. The mass spectra of dimers were obtained on a Finnigan MAT instrument [31]. Silica gel G Merck (0.040-0.063 mm) was used for column chromatographic separation of substances and for preparative thin layer chromatography (PTLC) as plates on an aluminum backing.

***trans* and *cis* Isomers of 1,2-Di(octaethyl-5-porphyrinyl)ethylene (IIa,b).** A. 1,2-Di(octaethyl-5-porphyrinyl)ethane (I) [8] (100 mg) was boiled in AcOH (75 ml) for 0.5 h, the mixture was cooled, water (100 ml) was added, the substance was extracted with chloroform, the organic layer was washed with water, evaporated to dryness, and the residue chromatographed on a column (3 $\times$ 15 cm) of silica gel in chloroform-ether (9:1) to separate the *trans* isomer (IIa), then in chloroform-ether (2:1) to elute the polar zone containing the *cis* isomer (IIb). After crystallization from chloroform-methanol (IIa) (26 mg, 26%) and (IIb) (57 mg, 57%) were obtained. Mass spectrum, m/z (%): 1092 (M^+ , 20), 546 (100).

PMR spectrum of (IIb): 9.69 (2H, s, $\text{CH}=\text{CH}$); 9.50 and 8.3 (2H and 4H, two s, 15,15' and 10,10', 20,20'-*meso* H); 4.28, 3.20, and 1.49 (20H, dq, dq, t, 3, 7, 3', 7'-4 $\times$ CH_2CH_3); 4.13, 3.91, and 1.88 (20H, dq, dq, t, 13,17,13',17'-4 $\times$ CH_2CH_3); 3.62, 3.33, and 1.49 (20H, dq, dq, t, 12,18,12',18'-4 $\times$ CH_2CH_3); 2.79, 2.55, and 0.75 (20H, dq, dq, t, 2,8,2'8'-4 $\times$ CH_2CH_3); -4.84 and -5.67 ppm (two s, NH).

In CD_3COOD : 10.23 (2H, $\text{CH}=\text{CH}$); 9.50 and 8.55 (2H and 4H, two s, *meso*-H); 4.57, 4.20, 4.00, 3.75, 3.51, and 3.40 (4H, 4H, 4H, 8H, 4H, 8H, all sextets, 16 $\times$ CH_2CH_3); 1.84, 1.62, 1.50, and 1.28 ppm (48H, all t, 16 $\times$ CH_2CH_3).

In CS_2 : 9.57 ($\text{CH}=\text{CH}$); 9.44 and 7.86 (2H, 4H, *meso*-H); 4.13, 4.06, 3.86, 3.54, 3.25, 3.00, 2.51, and 2.66 (each 4H, all sextets, CH_2CH_3); 1.88, 1.45, 1.445, and 0.58 (48H, all t, 16 $\times$ CH_2CH_3); -4.39 and -5.08 ppm (4H, NH).

PMR spectrum of complex (III) [23]: 9.87, 8.19 (2H, 4H, two s, *meso*-H); 5.22 (4H, br.s, CH_2CH_2 bridge); 4.30, 4.25, 3.90, 3.72, 3.35, 3.15, 2.65, and 2.40 (32H, all dq, 16 $\times$ CH_2CH_3); 1.95, 1.65, 1.47, and 1.08 ppm (48H, all t, 16 $\times$ CH_2CH_3). This spectrum is given for comparison with the spectrum of (IIb).

The PMR spectrum of the *trans* dimer (IIa) in CDCl_3 is given in [8].

B. Complex (IIa) (10 mg) in *o*-xylene (15 ml) was boiled for 1 h, the solution was evaporated to dryness in vacuum, the residue was chromatographed on a silica gel plate in chloroform-ether (9:1), and complex (IIa) (3-mg) and dimer (IIb) (4 mg) were obtained.

Copper Complex of *meso*-Formylcoproporphyrin-I Tetraethyl Ester (VI). A solution of complex (V) (1 g) [obtained in quantitative yield by heating porphyrin (IV) and copper acetate in chloroform] in dichloroethane (120 ml) was poured into the Vilsmeier complex from DMF (6 ml) and POCl_3 (5 ml). The mixture was heated at 65°C for 45 min, the solvent removed in vacuum, the oily residue was poured into cold water (200 ml) with vigorous stirring, the substance was extracted with chloroform (200 ml), and the chloroform layer washed with water. A solution of KOH (3 g) in water (50 ml) was added, the mixture boiled for 10 min, the organic layer separated, and chromatographed on a column (5 $\times$ 5 cm) of silica gel. The main fraction was evaporated in vacuum, the residue crystallized from a mixture of chloroform and ethanol, and complex (V) (800 mg, 79%) obtained.

Copper Complex of *meso*-Hydroxymethylcoproporphyrin-I Tetraethyl Ester (VII). A solution of NaBH₄ (300 mg) in MeOH (25 ml) was added to a solution of complex (VI) (800 mg) in chloroform (55 ml), the mixture was stirred for 15 min until the starting material was absent from the mixture, water (200 ml) was added, the mixture shaken, the organic layer separated, and chromatographed on a column (4 × 5 cm) of silica gel. The main fraction was evaporated, and the residue crystallized from a mixture of chloroform and ethanol. Complex (VII) (760 mg, 95%) was obtained.

Octaethyl Ester of 1,2-Di(*meso*-coproporphyrin-I-yl)ethane (IX). Complex (VII) (210 mg) was stored in TFA (1 ml) for 30 min, the solution was poured into water (50 ml), the substance was extracted with chloroform, the extract evaporated to dryness, and the residue chromatographed on a column (4 × 25 cm) of silica gel in CCl₄–ether (4:1, then 3:2). The dimeric complex (VIII) (55 mg) was eluted initially, and then unreacted complex (VII) (91 mg), which was subjected to a second treatment with TFA. A further 44 mg dimer (VIII) was isolated. The total yield of dimer (VIII) was 46%.

Dimer (VIII) (135 mg) was stored for 6 h in conc. H₂SO₄. The mixture was then poured onto finely ground ice (100 g), the mixture neutralized with aqueous ammonia, the substance extracted with chloroform, and chromatographed on a column (4 × 25 cm) of silica gel in chloroform–ether (10:1). Dimer (IX) (71 mg, 65%) was isolated. Mass spectrum, *m/z* (%): 1561 (M⁺, 50), 1489 (8), 794 (15), 780 (100), 766 (30), 708 (22), 694 (18). PMR spectrum: 9.85 (2H, s, 15,15'-H); 9.89, 8.54, 8.49, 8.10 (4H, all s, 10,10',20,20'-H); 5.55, 5.40, 5.12, 4.96 (4H, d, m, m, d, CH_2CH_2 ethane bridge, *J* = 9.7 Hz); 3.72, 3.70, 3.45, 3.38, 3.06, 2.74, 1.97, and 1.38 (24H, all s, 8 × CH₃ ring); signals from $\text{CH}_2\text{CH}_2\text{CO}$ and CH_2CH_3 formed numerous multiplets at 1.75–4.56 ppm; 1.15–1.26 (18H, overlapping t, 6 × CH₂CH₃); 1.03, 0.99 (6H, two t, 2 × CH₂CH₃); –3.90, –4.99, –5.01 ppm (4H, br.s, NH).

In *m*-xylene-D₁₀: 10.27 (2H, s, 15,15'-H); 9.37, 8.89, 8.87, and 8.28 (4H, all s, 10,10',20,20'-H); 5.90 and 5.40, 5.73, and 5.56 (4H, all m, CH_2CH_2 ethane bridge); 3.91 and 3.82, 3.65 and 3.56, 3.16 and 3.81, 2.12 and 1.45 ppm (24H, all s, 8 × CH₃ ring).

In CDCl₃ + CF₃COOD: 10.64 (2H, s, 15,15'-H); 10.28 (2H, s, 10,10'-H); 10.27 (2H, s, 20,20'-H); 5.98 (4H, br.s, CH_2CH_2 ethane bridge); 4.13–4.37 overlapping t and q, 3.91 t, 3.78 q, 3.20 t, 3.08 t, 2.78 t, 2.19 t (8 × $\text{CH}_2\text{CH}_2\text{CO}$ and 4 × CH₂CH₃); 3.55, 3.43, 3.39, 2.50 (all s, 8 × CH₃ ring); 1.33, 1.28, 1.16, 0.96 ppm (24H, all t, 8 × CH₂CH₃).

***trans* and *cis* Isomers of 1,2-Di(*meso*-coproporphyrin-I-yl)ethylene Octaethyl Ester (Xa) and (XIIa,b).** A. A solution of ethanedimer (IX) in AcOH (15 ml) was heated at 60°C for 1 h, then poured into water, the substance was extracted with chloroform, and chromatographed on a column (3 × 10 cm) of silica gel in chloroform–CCl₄–ether (2:3:1). The *trans* isomer (Xa) (19 mg) was isolated from the more mobile fraction after recrystallization from a mixture of chloroform and MeOH. The *cis* isomer (XIIa, b) (2 mg) was isolated from the less mobile fraction. Mass spectrum of (Xa), *m/z* (%): 1560 (M⁺, 100), 780 (40), 767 (35), 706 (25), 643 (10). Mass spectrum of (XIIa,b): *m/z* (%): 1560 (M⁺, 100), 780 (50). PMR spectrum of (Xa): 10.10, 10.09, 9.90 (2H, 2H, 2H, all s, *meso*-H); 8.52 (2H, s, CH=CH); 4.38–4.43 (overlapping t and m, 6 × CH₂CH₂CO); 4.26 and 2.42 (4H, 4H, two t, 2 × CH₂CH₂CO); 3.71, 3.67, 3.63, and 3.20 (24H, all s, CH₃ ring); 4.21–4.25 (12H, overlapping q, 6 × CH₂CH₃); 3.23–3.31 (12H, overlapping t, 6 × CH₂CH₂CO); 3.03 and –0.07 (10H, q and t, 2 × CH₂CH₃); 1.26, 1.24, 1.22 (all t, 6 × CH₂CH₃); –2.56 ppm (NH).

In CDCl₃ + 1% CF₃COOD: 10.54, 10.40, 10.21, 10.16 (8H, all s, *meso*-H and CH=CH); 4.26–4.39, 4.03 m, 3.59 m, 3.15 t, 3.08 t, 2.89 m (24H, 6 × CH₂CH₂CO); 3.52, 3.50, 3.38 (12H, 6H, 6H, all s, 8 × CH₃ ring); 2.31, 0.83 (10H, m and t, 2 × CH₂CH₃); 1.333, 1.31, 1.29 ppm (18H, all t, 6 × CH₂CH₃).

PMR spectrum of (XIIa): 9.72 (s, CH=CH); 9.59, 8.71, 7.30 (all s, *meso*-H); 3.61, 3.55, 3.30, 1.44 (all s, CH₃ ring); –4.90, and –5.70 ppm.

PMR spectrum of (XIIb): 9.70 (s, CH=CH); 9.60, 8.12, 7.93 (all s, *meso*-H); 3.63, 3.21, 3.07, 2.12 (all s, CH₃ ring); –4.70 and –5.53 ppm (two s, NH).

PMR spectrum of (XIIa,b): 2.0–4.50 (numerous groups of m, CH₂CH₂CO, CH₂CH₃); 1.05–1.28 ppm (overlapping t, CH₂CH₃).

B. *trans* Isomer (Xa) (9 mg) and *cis* isomer (XIIa,b) (15 mg) were obtained by boiling dimer (IX) (35 mg) in AcOH (15 ml) for 30 min and separating the product by PTLC on silica gel plates.

Zinc Complex of 1,2-Di(*meso*-coproporphyrin-I-yl)ethane Octamethyl Ester (XIX). A solution of the Cu complex (XIV) (500 mg) obtained in quantitative yield on treating porphyrin (XIII) with copper acetate in chloroform–methanol was poured into the complex obtained from POCl₃ (3 ml) and DMF (3 ml). The reaction mixture was stirred at 60°C for 30 min, the solvent evaporated in vacuum, and finely crushed ice (100 g) was added rapidly with vigorous stirring to the oily residue. After 10 min, the precipitate of phosphorus complex was filtered off and dissolved in methanol (50 ml). The solution was heated to 40°C, and NaOH (500 mg) in water (10 ml) added dropwise with stirring during 5 min. After 30 min, the precipitate

of red complex (XV) was filtered off, washed with water, dried, dissolved in chloroform (20 ml), filtered through a layer (1 cm) of silica gel, and the solvent evaporated. The residue was dissolved in dichloromethane (20 ml), and a rapidly prepared solution of NaBH_4 (150 mg) in methanol (5 ml) was added to it at once. The mixture was stirred for 20 min until completion of the reduction reaction, water (100 ml) added, the organic layer was separated, filtered through a layer (1 cm) of aluminum oxide, and evaporated to dryness. Complex (XVI) (420 mg) was obtained. Trifluoroacetic acid (2 ml) was added to complex (XVI) (400 mg), which had been carefully dried in vacuum, the mixture was shaken vigorously for 15 min, and then evaporated to dryness in vacuum. The residue was dissolved in chloroform (80 ml), the solution washed with water, and dimer (XVII) (180 mg) isolated chromatographically on a column (3 $\times$ 10 cm) of silica gel. Dimer (XVIII) (120 mg) was obtained from (XVII) by demetallation for 6 h in conc. H_2SO_4 (20 ml). Heating dimer (XVIII) with zinc acetate (240 mg) in a mixture (40 ml) of chloroform and methanol (9:1) with subsequent chromatographic purification on a column (3 $\times$ 15 cm) of silica gel (chloroform-ether, 9:1) gave the biszinc complex (XIX) in quantitative yield. PMR spectrum of dimer (XVIII): 9.88, 9.87, 8.71, 8.56, 8.50, and 8.29 (6H, all s, *meso*-H); -3.82, -3.90, -4.92, and -5.02 ppm (4H, all s, NH).

PMR spectrum of dimer (XIX) in $\text{C}_5\text{D}_5\text{N}$: 9.87, 9.85, 9.80 ppm (2H, 2H, 2H, all s, *meso*-H); the protons of the remaining substituents were displayed as groups of signals in the 1.1-4.5 ppm region.

Nickel Complex of 1,2-Di(*meso*-coproporphyrin-I-yl)ethane Octaisopropyl Ester (XXIII). A. Phosphorus oxychloride (1 ml) was added to a solution of complex (XXI) (100 mg) in a mixture of dichloromethane (50 ml) and DMF (1 ml), the solution was stirred at 40°C for 1.5 h, washed with water, concentrated, diluted with methanol (40 ml), NaBH_4 (50 mg) was added, and the mixture stirred for 15 min, and washed with water. The substance was extracted with chloroform, the solution evaporated, and the residue chromatographed on a column (3 $\times$ 10 cm) of silica gel. The main substance was eluted with a dichloromethane-methanol (19:1) mixture, the solvent evaporated in vacuum, and complex (XXII) (87 mg, 82%) obtained. UV spectrum in chloroform, λ_{max} ($\epsilon \times 10^{-3}$): 410 (210), 539 (11.5), 578 nm (16.8). PMR spectrum: 9.42, 9.39, 9.37 (3H, all s, *meso*-H); 5.02-5.22 (6H, overlapping m, CH_2NMe_2 , CHMe_2); 4.05-4.20 (8H, m, $\text{CH}_2\text{CH}_2\text{CO}$); 3.46, 3.38, 3.37, 3.32 (12H, all s, CH_3 ring); 2.90-3.20 (8H, m, $\text{CH}_2\text{CH}_2\text{CO}$); 1.36 (6H, s, NMe_2); 1.15-1.32 ppm (24H, overlapping d, CHMe_2).

B. A mixture of complex (XXII) (100 mg) in dichloromethane (10 ml) and MeI (10 ml) was boiled for 2 h and then evaporated to dryness. The residue was chromatographed on a column (3 $\times$ 30 cm) of silica gel initially in dichloromethane-hexane (4:1) to remove less polar products and then in dichloromethane-ether (9:1). The principal fraction was separated, evaporated to dryness, dissolved in dichloromethane (0.1 ml), methanol (15 ml) added, and the mixture stored in the refrigerator for several days. Complex (XXIII) (45 mg) was isolated as well-formed crystals. UV spectrum in chloroform, λ_{max} ($\epsilon \times 10^{-3}$): 405 (180), 543 (16.5), 574 nm (21.5).

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