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Spectral properties of porphyrins and their precursors and derivatives

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Abstract. The data of IR, ^{1}H NMR and electronic absorption spectroscopy of porphyrins and their precursors and derivatives are analysed, systematised and generalised. The bibliography includes 105 references.

I. Introduction

Problems of spectroscopy of porphyrins have been considered in detail in a number of papers and monographs (see, for example, Refs 1 – 8). However, the last 10 – 15 years have been marked by impressive progress in the synthetic chemistry of porphyrins resulting in the determination of the spectral characteristics of new heterocyclic compounds (porphyrins and their intermediates) with very complex structures. It should be noted that most studies dealt with the spectra of particular porphyrins and their precursors with the aim of establishing the structures of the newly synthesised compounds. However, the results of investigations by different spectral methods, which were performed under different conditions and using a limited number of compounds, cannot necessarily be compared.

In order for the relationship between the structure and the spectral properties of complex multicontour chromophores (among which are, undoubtedly, porphyrins) to be revealed, comprehensive investigation of a diversity of compounds whose structures vary from simple to complex must be carried out. Pyrrole intermediates are of obvious interest because they can be used to follow changes in the spectral characteristics as the macrocycle undergoes chemical modifications. In the present review, we analyse, systematise and generalise the recent data of IR, ^{1}H NMR and electronic absorption spectroscopy of porphyrins and their derivatives and precursors, *viz*., of mono-, di- and tetrapyrrole compounds.

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II. IR spectra of porphyrins and their precursors and derivatives

IR spectroscopy enables one not only to identify compounds, but also to follow changes in various characteristics of individual chemical bonds and the molecule as a whole that occur upon chemical modifications. For example, information on the relative stabilities of corresponding chemical bonds in the molecules can be obtained by comparing the force constants of these bonds, which can be calculated from the spectral data. Since all force constants cannot necessarily be determined from the spectral data, qualitative conclusions about the relative stabilities of the bonds are often made based on the experimental vibration frequencies observed in IR spectra. These frequencies are functions of the atomic weights and the force constants of the bonds. A comparison of the frequencies of analogous vibrations for different compounds can be performed only in the case of the characteristic vibrations. The shifts of characteristic vibration frequencies are directly related to the changes in the electronic states of the bonds and the fragments within which the vibrations under consideration are localised.

Investigation of a large number of structurally similar molecules can be a help in refining the assignment of vibrations to particular fragments of the porphyrin ring.

1. Pyrroles

The assignment of virtually all bands in the IR spectrum of pyrrole (**1a**) was made[9,10] and this spectrum can be used in studies of pyrrole derivatives (Table 1). The NH stretching vibrations in the spectrum of solid pyrrole are observed in the region of $\sim$3500 cm^{-1}. In chloroform, this band is split into two components (at 3400 and 3497 cm^{-1}). The intensity of the band at 3497 cm^{-1} increases upon dilution. Therefore, the band at 3400 cm^{-1} corresponds to associated NH bonds, whereas the band at 3497 cm^{-1} is assigned to the free bonds. According to the results of calculations carried out for the isolated pyrrole molecule, the NH stretching vibration band in its spectrum is located at 3491 cm^{-1} (Table 2).

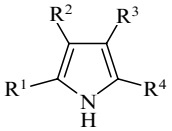
Two pronounced bands at 3100 and 3130 cm^{-1} are assigned to CH stretching vibrations of pyrrole. Calculations by the semiempirical PM3 method demonstrated[11] (see Table 2) that the more intense band (at 3100 cm^{-1}) corresponds to vibrations of the C(α)–H bonds, whereas the less intense band corresponds to vibrations of the C(β)–H bonds. The frequencies in the region of 1350 – 1600 cm^{-1} belong to skeletal vibrations of pyrrole. In the spectrum, these vibrations are observed as an intense band at 1350 cm^{-1} and a medium intensity band at 1530 cm^{-1}.

Table 1. Positions of the absorption maxima (cm^{-1}) in the IR spectra of the pyrroles **1a**–**l** (in KBr pellets).[9, 10]

Compound **1**	Pyrrole fragment			Alkyl substituent		ν(C=O)	ν(C–O)
	ν(NH)	ν(CH)	ν(C–C)	δ(CH)	γ(CH)		
a[a]	3495	3100, 3130	1350, 1530	–	–	–	–
b	3458	–	1350, 1508	1380	1004	1667	1284
c	3456	–	1348, 1510	1379	1022	1664	1290
d	3458	–	1346, 1515	1386	1018	1680	1290
e	3450	–	1360, 1530	1380	1010	1670	1280
f	3451	–	1338, 1514	1380	1015	1690	1287
g	3450	–	1328, 1517	1377	1090	1685	1273
h	3453	–	1316, 1514	1378	1065	1702	1255
i	3452	–	1320, 1517	1384	1116	1687	1268
j	3466	–	1384, 1540	1370	1088	1686	1265
k	3450	–	1357, 1578	1382	1000	1680	1295
l	3454	3108	1352, 1564	1378	994	1637	1290

[a] According to the published data.[2]

Examinations[9–12] of the spectra of substituted pyrroles **1b**–**l** demonstrated that chemical modifications of the molecule lead to essential spectral changes. Thus, the spectrum of 2-ethoxycarbonyl-3,4,5-trimethylpyrrole (**1b**) shows CH deformation vibrations of the alkyl groups.



1a–**l**

Compound **1**	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	Me	Me	CO_2Et
c	Me	Et	Me	CO_2Et
d	Me	Bu^n	Me	CO_2Et
e	Me	Bu^n	Me	CO_2Bn
f	Me	Et	Me	CO_2Bn
g	CO_2Et	Et	Me	CO_2Bn
h	CO_2Et	Et	Me	CO_2H
i	CO_2H	Et	Me	CO_2Et
j	CO_2Et	Et	Me	I
k	I	Et	Me	CO_2Et
l	H	Bu^n	Me	CO_2Et
m	H	Me	Me	H
n	Me	H	H	Me
o	Me	Me	Me	H
p	H	Me	Et	Me
q	H	Me	Et	CO_2Et
r	Me	Et	Me	CHO
s	Me	Me	Et	CHO

The skeletal vibration bands are shifted to the lower-frequency region and are more intense than the corresponding bands in the spectrum of unsubstituted pyrrole. Apparently, a rise in the intensities of these bands can be accounted for by the effect of the electron-withdrawing ester group.

This assumption is supported by the following fact. In the spectrum of 2-benzyloxycarbonyl-5-ethoxycarbonyl-4-ethyl-3-methylpyrrole (**1g**), the vibration bands of the pyrrole ring are shifted further to the low-frequency region with a simultaneous increase in their intensities. Of the molecules under consideration, the largest low-frequency shifts of skeletal vibrations are observed for the α-carboxypyrroles **1h**,**i**. Noteworthy are also the low-frequency shifts of NH vibrations of these pyrroles. The spectrum of 4-butyl-2-ethoxycarbonyl-3-methylpyrrole (**1l**) has an intense band at 3108 cm^{-1} corresponding to CH stretching vibrations of the pyrrole ring. Investigations demonstrated that this band corresponds to vibrations of the C(α)–H bond of pyrrole (the β positions are occupied by substituents). The spectral characteristics of the positional isomers **1h**,**i** and **1j**,**k** differ only slightly from each other. An increase in the size of the alkyl substituent (R) in 4-R-2-ethoxycarbonyl-3,5-dimethylpyrroles **1b**–**d** (R = Me, Et or Bu^n) is accompanied primarily by an increase in the intensity of the CH vibration bands of the alkyl groups. It should be noted that the C=O, C–O, C–OH and C–I vibrations are characteristic. The bands belonging to these vibrations are present in the spectra of all compounds of the series **1b**–**l** and allow one to

Table 2. Vibration frequencies (cm^{-1}) in the IR spectra of the pyrroles **1a**–**l** calculated by the PM3 method.[11]

Compound **1**	Pyrrole fragment			Alkyl substituent		ν(C–O)
	ν(NH)	ν(CH)	ν(C–C)	δ(CH)	γ(CH)	
a	3491	3100, 3133	1355, 1530	–	–	–
b	3453	–	1350, 1512	1384, 1390	1007	1289
c	3459	–	1356, 1516	1386, 1399	1027	1293
d	3462	–	1348, 1510	1382, 1394	1021	1296
e	3447	–	1364, 1528	1380, 1392	1012	1284
f	3453	–	1340, 1516	1380, 1391	1011	1280
g	3450	–	1325, 1515	1379, 1395	1094	1278
h	3450	–	1320, 1510	1376, 1397	1069	1252
i	3448	–	1316, 1519	1380, 1391	1119	1270
j	3466	–	1386, 1544	1373, 1389	1086	1266
k	3454	–	1350, 1576	1376, 1382	1002	1290
l	3456	3112	1354, 1564	1371, 1384	994	1284

identify the pyrrole synthesised and to establish its structure and purity.

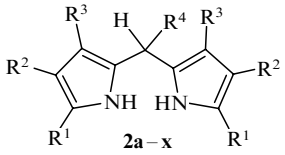
2. Dipyrrolylmethanes

The IR spectra of dipyrrolylmethanes **2a**–**x** were measured and examined.[12–14] The structures of these compounds have been previously investigated by calculation methods (the MM + molecular mechanics method and the semiempirical PM3 method). The calculated energy parameters and geometric characteristics corresponding to the energy minima are summarised in the studies.[15,16] The energy parameters of the dipyrrolylmethane molecule are substantially affected by the substituents at positions 5 and 5′, while the effects of the alkyl substituents at positions 3, 3′, 4 and 4′ are insignificant.

As mentioned above, the NH stretching vibrations of pyrrole are observed at 3495 cm^{-1}. On going to dipyrrolylmethane (**2x**), the NH vibration band is shifted to the low-frequency region by $\sim$40 cm^{-1}. Introduction of the phenyl substituent at the *meso*-position of dipyrrolylmethane (the compound **2w**) leads to a further short-wavelength shift (by 15 cm^{-1}) of this band (Table 3). Below are given the charge distributions on the atoms of the dipyrrolylmethane molecules, which show the influence of the electronic factors upon chemical modifications of the molecule.

Thus, the presence of electron-withdrawing substituents (for example, the carboxy group) at positions 5 and 5′ of dipyrrolylmethane leads to a decrease in the electron density on the nitrogen atoms (the compound **2b**), which is accompanied by lowering of the ν(NH) frequency by $\sim$40 cm^{-1} (Tables 3 and 4). The presence of the electron-donating methoxy groups in the *meso* substituents of the carboxy derivatives **2n**,**p**,**r** causes a high-frequency shift (by $\sim$15 cm^{-1}) of the NH vibration band compared to that in the spectrum of the carboxy derivative **2b**. The larger the electron density on the nitrogen atom, the higher the vibration frequency.

Compound	Charges on atoms (arb.u.)				
	N(1)	C(2)	C(3)	C(4)	C(5)
1a	0.337	−0.315	−0.162	−0.164	−0.309
2a	0.368	−0.296	−0.159	−0.101	−0.331
2b	0.425	−0.279	−0.184	−0.068	−0.358
2f	0.339	−0.312	−0.133	−0.133	−0.312
2w	0.387	−0.305	−0.164	−0.164	−0.311



2a–**x**

Compound **2**	R^1	R^2	R^3	R^4
a	CO_2Et	Me	Me	H
b	CO_2H	Bu^n	Me	H
c	CO_2Et	Et	Me	H
d	CO_2Et	Bu^n	Me	H
e	H	Me	Me	H
f	CO_2Et	H	Me	H
g	H	Me	Bu^n	H
h	CO_2H	Me	Bu^n	Ph
i	CO_2H	Bu^n	Me	Ph
j	COH	Me	Bu^n	Ph
k	CO_2Et	Bu^n	Me	Ph
l	CO_2Et	Me	Bu^n	Ph
m	H	Me	Bu^n	4-$MeOC_6H_4$
n	CO_2H	Me	Bu^n	4-$MeOC_6H_4$
o	H	Me	Bu^n	3-$MeOC_6H_4$
p	CO_2H	Me	Bu^n	3-$MeOC_6H_4$
q	H	Me	Bu^n	2-$MeOC_6H_4$
r	CO_2H	Me	Bu^n	2-$MeOC_6H_4$
s	H	Me	Bu^n	4-$NO_2C_6H_4$
t	CO_2H	Me	Bu^n	4-$NO_2C_6H_4$
u	H	Me	Bu^n	3-$NO_2C_6H_4$
v	CO_2H	Me	Bu^n	3-$NO_2C_6H_4$
w	H	H	H	Ph
x	H	H	H	H

The intense band at 3100 cm^{-1} was assigned[12] to CH stretching vibrations of pyrrole [C(α)–H stretching vibrations]. The formation of the dipyrrole structure is accompanied by the high-frequency shift of this band by $\sim$20 cm^{-1} (see Table 3). The introduction of the aryl substituent at the *meso* position of dipyrrolylmethane has virtually no effect on CH vibrations of the pyrrole rings. The spectral characteristics of the positional isomers **2h**,**i** are very similar (see Table 4).

The intense band at 1350 cm^{-1} and the medium intensity band at 1530 cm^{-1} belong to skeletal vibrations of pyrrole. In the dipyrrolylmethane **2w**, the C–C vibration frequency of the pyrrole fragment is shifted to the low-frequency region by $\sim$5 cm^{-1}. Alkylation of the pyrrole rings and the replacement

Table 3. Positions of the absorption maxima (cm^{-1}) in the IR spectra of the pyrrole **1a** and the dipyrrolylmethanes **2c**–**g**,**m**,**o**,**q**,**s**,**u**,**w**,**x**.[12–14]

Compound	ν(NH)		ν(CH)		ν(C–C)[a]		ν(C–C)[b]	
	A	B	A	B	A	B	A	B
1a	3491	3495	3100, 3133	3100, 3130	1355, 1530	1350, 1530	–	–
2c	3448	3452	3124	3120	1335, 1517	1335, 1520	1364	1370
2d	3436	3432	3122	3125	1333, 1514	1330, 1525	1362	1370
2e	3446	3444	3123	3120	1330, 1507	1335, 1520	1364	1375
2f	3433	3430	3122	3125	1325, 1510	1330, 1520	1360	1380
2g	3434	3440	3123	3120	1325, 1512	1330, 1530	1360	1380
2m	3428	3430	3121	3120	1328, 1518	1330, 1530	1358	1360
2o	3432	3430	3121	3120	1324, 1520	1325, 1540	1358	1360
2q	3426	3421	3120	3122	1325, 1515	1330, 1525	1360	1365
2s	3448	3442	3122	3124	1326, 1521	1330, 1527	1362	1368
2u	3442	3440	3124	3128	1328, 1518	1330, 1530	1360	1360
2w	3438	3440	3124, 3166	3129, 3170	1346, 1525	1350, 1540	1362	1370
2x	3453	3455	3122, 3160	3122, 3160	1345, 1524	1330, 1530	1359	1360

Note. Here and in Tables 4 and 5, the calculated and experimental (in KBr pellets) spectra are denoted by A and B, respectively.
[a] Stretching vibrations of the pyrrole fragment; [b] stretching vibrations of the methine bridge.

Table 4. Positions of the absorption maxima (cm^{-1}) in the IR spectra of the dipyrrolylmethanes **2b**,**h**–**l**,**n**,**p**,**r**,**t**,**v**.[15, 16]

Compound **2**	ν(NH)		ν(C–C) [a]		ν(C–C) [b]		ν(C=O)
	A	B	A	B	A	B	B
b	3416	3412	1310, 1520	1315, 1520	1354	1360	1675
h	3418	3410	1318, 1512	1321, 1510	1350	1358	1670
i	3421	3427	1320, 1522	1326, 1510	1354	1357	1685
j	3438	3435	1323, 1517	1332, 1510	1350	1355	1670
k	3444	3440	1322, 1520	1330, 1510	1350	1360	1675
l	3452	3445	1326, 1525	1330, 1514	1356	1360	1680
n	3430	3427	1330, 1515	1335, 1520	1360	1366	1685
p	3432	3429	1324, 1522	1330, 1530	1362	1365	1680
r	3433	3427	1320, 1524	1324, 1520	1356	1350	1690
t	3429	3434	1324, 1618	1329, 1522	1340	1342	1675
v	3433	3438	1319, 1520	1324, 1530	1342	1340	1678

[a] Stretching vibrations of the pyrrole fragment; [b] stretching vibrations of the methine bridge.

of one of the *meso*-hydrogen atoms by the aryl group are accompanied by an increase in this shift (see Tables 3 and 4). The presence of electron-withdrawing substituents at positions 5 and 5′ of dipyrrolylmethane leads to lowering of the ν(C–C) frequency of the pyrrole fragment compared to that in the spectrum of unsubstituted dipyrrolylmethane.

Calculations of the spectra of dipyrrolylmethanes demonstrated that the intense band in the region of 1340–1365 cm^{-1} corresponds to C–C vibrations of the methane bridge. The presence of the electron-withdrawing nitro groups in the aryl *meso*-substituents leads to a substantial increase in the intensity of this band.

On going from pyrroles to dipyrrolylmethanes, the C=O, C–O and C–OH vibrations remain characteristic and allow the identification of the dipyrrolylmethane synthesised. It can be seen from the data presented in Tables 1–4 that the IR spectra of pyrroles differ substantially from those of dipyrrolylmethanes. The involvement of pyrrole in the open conjugated system of hexamethyldipyrrolylmethene as well as in the cyclic octamethylporphyrinogen system [7] is accompanied by further complications of the spectra. However, the most pronounced effect is observed when pyrrole is involved in the conjugated porphyrin macrocycle.

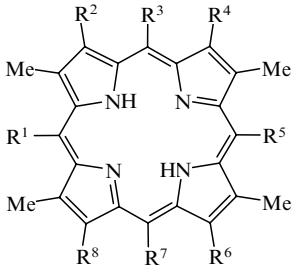
3. Porphyrins

The effects caused by an increase of the molecular symmetry (for example, upon formation of metal complexes) or its lowering (for example, in the case of introduction of substituents in the macrocycle) are manifested in the IR spectra of porphyrins along with the changes in stretching vibration frequencies.

When studying these effects, it is useful to consider two series of compounds: (1) porphyrins containing the hydrogen atoms at the *meso* positions of the macrocycle and substituents at the β positions of the pyrrole fragments and (2) porphyrins containing substituents at the *meso* positions and the hydrogen atoms at the β positions of the pyrrole fragments.

The IR spectra of β-alkylated porphyrins **3a**–**w** in which two and four *meso*-hydrogen atoms are successively replaced by the alkyl (CH_3–C_6H_{13} or $C_{11}H_{23}$), phenyl or aryl (C_6H_4X, X = H, 4-OMe, 3-OMe, 2-OMe, 4-NO_2 or 3-NO_2) substituents were investigated.[14, 17–21]

The geometric and energy parameters of the porphyrin molecules corresponding to the energy minima are summarised in the studies.[22, 23] The experimental vibration frequencies of the porphyrins **3a**–**w** and those calculated by the PM3 method are given in Table 5. The *meso*-alkyl substituents in the porphyrins **3a**–**g** can adopt various conformations. However, calculations by the semiempirical PM3 method demonstrated [24] that the extended zigzag chain typical of n-alkanes in the crystalline state is a preferential conformation of the alkyl substituents. The cisoid and transoid relative arrangements of the alkyl substituents at positions 5 and 15 are equally probable. The corresponding conformers shown in Fig. 1 *a*,*b* have equal energies of steric strain (365 kJ mol^{-1}). The *meso*-phenyl or *meso*-aryl substituents in the porphyrins **3h**–**s** are located perpendicular to the plane of the porphyrin macrocycle (Fig. 1 *c*,*d*).[22]



3a–**w**

Compound **3**	R^1, R^5	R^2, R^4, R^6, R^8	R^3, R^7
a	Me	Me	H
b	Et	Me	H
c	Pr^n	Me	H
d	Bu^n	Me	H
e	C_5H_{11}	Me	H
f	C_6H_{13}	Me	H
g	$C_{11}H_{23}$	Me	H
h	Ph	Bu^n	H
i	4-$OMeC_6H_4$	Bu^n	H
j	3-$OMeC_6H_4$	Bu^n	H
k	2-$OMeC_6H_4$	Bu^n	H
l	4-$NO_2C_6H_4$	Bu^n	H
m	3-$NO_2C_6H_4$	Bu^n	H
n	H	Bu^n	Ph
o	H	Bu^n	4-$OMeC_6H_4$
p	H	Bu^n	3-$OMeC_6H_4$
q	H	Bu^n	2-$OMeC_6H_4$
r	H	Bu^n	4-$NO_2C_6H_4$
s	H	Bu^n	3-$NO_2C_6H_4$
t	H	Bu^n	H
u	Et	Me	Ph
v	C_6H_{13}	Me	Ph
w	C_6H_{13}	Me	4-$OMeC_6H_4$

The out-of-plane CH deformation vibrations of porphyrins are observed in the region of 830–850 cm^{-1}. Among these are the CH vibrations of the pyrrole rings and methine bridges of the macrocycle. The γ(CH) vibration frequency of the pyrrole fragments of porphyrins increases compared to the corresponsing frequency in the spectrum of pyrrole as the interactions between

Table 5. The NH and CH vibration frequencies (cm^{-1}) of the porphyrin ring in the β-octaalkylporphyrins **3a**–**w**.[14, 17, 24]

Compound **3**	ν(NH)		δ(NH)		γ(NH)		ν(CH) [a]		δ(CH) [b]		γ(CH) [c]	
	A	B	A	B	A	B	A	B	A	B	A	B
a	3348	3346	980	960	708	695	3022	3027	1507	1502	830	832
b	3343	3342	974	963	707	695	3011	3016	1487	1497	825	832
c	3342	3340	986	964	710	700	3002	3008	1483	1491	829	834
d	3346	3345	992	970	712	700	2942	2940	1479	1484	835	836
e	3348	3346	1001	978	714	705	2926	2920	1480	1486	831	836
f	3347	3348	991	984	715	705	2907	2900	1478	1489	832	837
g	3352	3350	1003	980	721	710	2906	2880	1477	1486	833	838
h	3323	3320	992	980	720	700	2960	2960	1485	1488	840	842
i	3321	3315	1007	990	714	709	3006	3000	1484	1490	845	849
j	3323	3318	974	965	717	702	2984	2980	1478	1487	840	845
k	3332	3320	970	960	710	700	2970	2962	1481	1486	839	844
l	3325	3310	994	985	715	710	3025	3030	1494	1500	850	853
m	3332	3320	996	980	719	705	2994	2990	1479	1485	845	848
n	3327	3327	997	960	700	690	2884	2990	1490	1489	830	840
o	3318	3315	1005	986	718	706	2986	3010	1490	1500	845	850
p	3328	3320	994	978	704	690	3012	2940	1479	1485	830	840
q	3330	3324	981	970	705	690	2942	2920	1492	1500	849	852
r	3319	3310	1002	990	721	710	2931	3020	1493	1500	842	846
s	3336	3324	994	980	731	704	3014	2995	1479	1486	839	844
t	3338	3335	990	984	714	702	2994	2980	1476	1484	835	844
u	3342	3325	1010	974	728	710	3007	3060	1492	1500	–	–
v	3340	3328	1013	982	730	705	3028	3048	1484	1496	–	–
w	3347	3330	1017	990	728	700	3020	3035	1480	1492	–	–

[a] Stretching vibrations of the alkyl groups; [b] deformation vibrations of the alkyl groups; [c] out-of-plane deformation vibrations of the methine bridges.

the C(β)–C(β) bonds and the π-system of the macrocycle are weakened due to the introduction of alkyl or aryl substituents.

In the spectra of β-unsubstituted porphyrins (*meso*-tetraalkyl- and -tetraphenylporphyrins), an intense band in the region of 772–805 cm^{-1} corresponds to γ(CH) vibrations. This band is absent in the spectra of octamethyl-, octaethyl-, dodecaalkyl- and dodecaphenylporphyrins.[25–27] The γ(CH) vibration frequency depends substantially on the presence of substituents at the *meso* positions of the macrocycle. Thus, the bands at 772 and 780 cm^{-1} correspond to these vibrations in the spectra of porphyrin and *meso*-tetra(*iso*-butyl)porphyrin, respectively. This effect is more pronounced in the spectrum of tetraphenylporphyrin in which the γ(CH) vibration band is observed at 797 cm^{-1}.[25]

In the IR spectrum of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**3t**), out-of-plane C(β)–H deformation vibration bands are absent, whereas an intense band at 835 cm^{-1} belongs to γ(CH) vibrations of the *meso*-hydrogen atoms (see Table 5). This band is absent in the spectra of the 5,15-dialkyl-10,20-diphenylporphyrins **3u**–**w**, whereas it is observed in the region of ~830–850 cm^{-1} in the spectra of the 5,15-dialkyl- and 5,15-diaryl-β-octaalkylporphyrins **3a**–**m**.

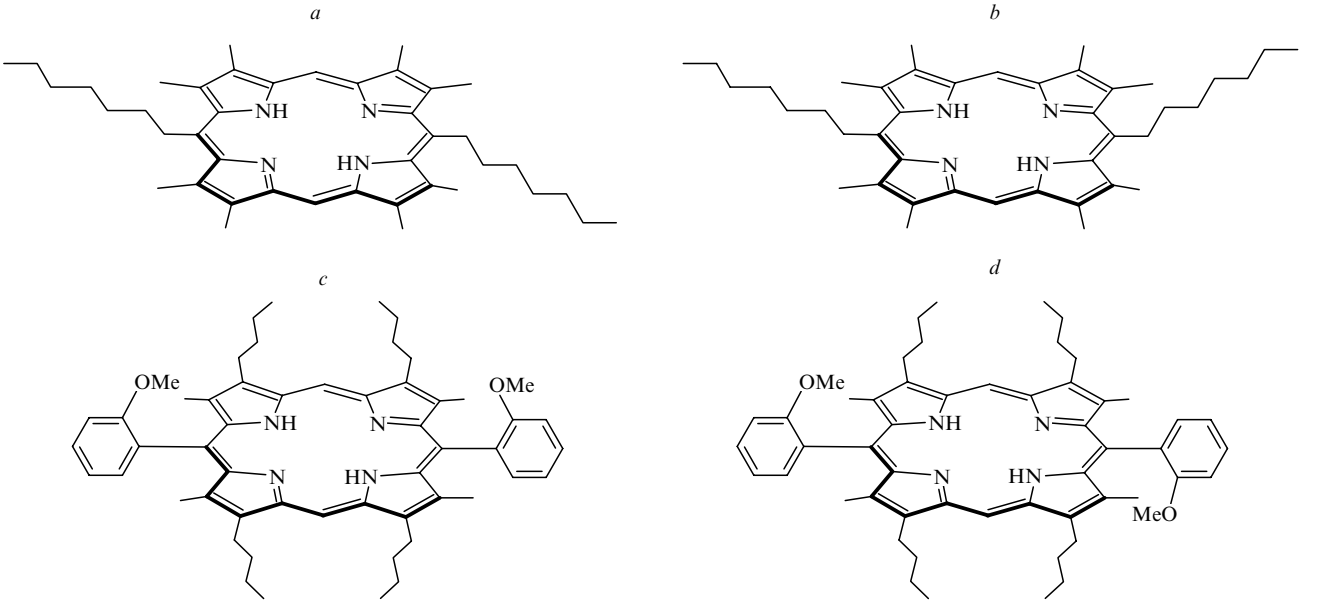


Figure 1. Cisoid (*a*) and transoid (*b*) conformers of 5,15-di-n-heptyl-2,3,7,8,12,13,17,18-octamethylporphyrin and the atropoisomers [α,α (*c*) and α,β (*d*)] of 2,8,12,18-tetrabutyl-5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethylporphyrin.[22]

Table 6. The CH vibration frequencies (cm^{-1}) of the phenyl groups in the diphenyl(aryl)octaalkylporphyrins **3h**–**m**,**o**–**w** (in KBr pellets).[4, 18]

Compound **3**	γ(C(1)–H)	γ(C(2)–H)	γ(C(3)–H)	γ(C(4)–H)	γ(C(5)–H)	δ(CH)
h	–	–	–	–	745	1170, 1050
i	–	840	–	–	–	1174, 1065
j	870	–	780	–	–	1164, 1060
k	–	–	–	750	–	1179, 1050
l	–	846	–	–	–	1185, 1069
m	890	–	785	–	–	1162, 1071
o	–	844	–	–	–	1180, 1068
p	874	–	782	–	–	1170, 1067
q	–	–	–	754	–	1180, 1055
r	–	848	–	–	–	1184, 1073
s	896	–	787	–	–	1170, 1068
u	–	–	–	–	747	1172, 1060
v	–	–	–	–	750	1178, 1050
w	–	840	–	–	–	1174, 1075

Since the out-of-plane deformation vibrations of the adjacent CH bonds of the phenyl fragments, which occur in phase, strongly interact with each other, the positions of the corresponding bands in the spectra depend on the number of the above-mentioned bonds. These bands are intense and can be used for the determination of the position of the substituent in the phenyl fragment (Table 6).

The spectra of the 5,15-diphenylporphyrins **3h**,**n** have an intense band at 745 cm^{-1} due to interactions between five adjacent CH bonds (for example, in monosubstituted benzene).[25] The spectra of the di(*meta*-R-phenyl)porphyrins **3j**,**m**,**p**,**s** have bands in the regions of 780–787 cm^{-1} (three adjacent CH bonds) and 870–896 cm^{-1} (one CH bond). The spectra of the di(*ortho*-R-phenyl)porphyrins **3k**,**q** have a band at ~750 cm^{-1} (four adjacent CH bonds), whereas the spectra of the di(*para*-R-phenyl)porphyrins **3i**,**l**,**o**,**r** have a band in the region of 840–848 cm^{-1} (two adjacent CH bonds) (see Table 6).

The identification of in-plane CH deformation vibrations presents a more complicated problem. The bands in the region of 964–1060 cm^{-1} are generally assigned[28] to δ(CH) vibrations of the pyrrole fragments of porphyrins. These bands are observed as two narrow closely spaced intense bands. The spectra of β-octaalkylporphyrins have no intense bands in this region. The medium intensity bands in the region of 1484–1500 cm^{-1} belong to δ(CH) vibrations of alkyl groups. Their positions remain virtually unchanged as the length of the alkyl substituent increases (see Table 5). The in-plane CH deformation vibrations of the phenyl fragments are observed in the region of 1000–1300 cm^{-1}.[25] In the spectra of *meso*-diphenyloctaalkylporphyrins, these vibrations are observed as medium intensity bands at 1170 and 1050 cm^{-1}, which are insignificantly shifted upon introduction of electron-withdrawing or electron-donating substituents into the benzene rings (see Table 6). The spectra of the positional isomers **3h**,**n** are similar. In the spectra of tetraphenylporphyrins, the ν(CH) vibrations of the phenyl substituents are observed at 3100 cm^{-1}. Therefore, it is conceivable that the band at 3000 cm^{-1} has a complex nature because the CH vibrations of both the porphyrin and benzene rings are observed in this region. The spectra of the β-alkylated porphyrins **3a**–**m**,**u**–**w** have bands in the region of 2940 cm^{-1}, which, apparently, belong to CH stretching vibrations of the alkyl groups.

The skeletal vibrations of the porphyrin ring are observed in the region of 1100–1250 cm^{-1}.[24, 26] The IR spectra of the β-octaalkylporphyrin **3t** and the 5,15-dialkyl-β-octamethylporphyrins **3a**–**g** have several medium intensity bands in this region. The assignment of the skeletal vibration bands in the spectra of *meso*-phenyl-substituted porphyrins is hampered by the fact that vibrations of the porphyrin ring overlap with those of the benzene fragments. The bands in the region of 1350–1600 cm^{-1} were assigned to ν(C–C) vibrations of the benzene rings.[26] In the spectrum of *meso*-tetraphenylporphyrin, these vibrations are manifested as three rather weak bands (at 1489, 1570 and 1590 cm^{-1}) whose intensities become higher as the frequency increases. It is known[29] that the ratio of the intensities of these bands in the spectra of functional benzene derivatives is determined by the presence or absence of conjugation between the phenyl fragments and functional groups. In the spectrum of *meso*-tetraphenylporphyrin, alternation of the intensities of the bands is analogous to that observed in the spectrum of biphenyl.

Chemical modifications of the phenyl substituents in *meso*-phenyl-substituted porphyrins exert a substantial effect on the skeletal vibrations of the macrocycle.[25, 26] Tetra(*ortho*- and *meta*-R-phenyl)porphyrins exist as two atropoisomers due to which the band at 1200 cm^{-1} is split. The spectra of tetra(*para*-R-phenyl)-porphyrins have one intense band at about 1100 cm^{-1}, which is shifted to the low-frequency region in parallel with the increase in the mass of the substituent. The spectra of the di(*ortho*- and *meta*-R-phenyl)porphyrins **3j**,**k**,**m**,**p**,**q**,**s** have a pronounced doublet at 1200 cm^{-1}, whereas the spectra of the *para*-derivatives **3i**,**l**,**o**,**r** show an intense band at 1100 cm^{-1} (for the nitro derivatives) or at 1180 cm^{-1} (for the methoxy derivatives).

Since the nitrogen atoms in porphyrins are more electronegative than those in pyrroles, the N–H bond length (90 pm) in porphyrins is 10% smaller than that in pyrrole. Because of this, the bands at 719 and 725 cm^{-1} (which are 160 cm^{-1} higher than those in the case of pyrrole) are assigned to out-of-plane γ(NH) deformation vibrations of the porphyrin molecule, while the bands at 970 and 980 cm^{-1} (which are 160 cm^{-1} lower than those in the case of pyrrole) are assigned to in-plane δ(NH) deformation vibrations.[26, 30] The validity of this assignment is additionally confirmed by the absence of the corresponding bands in the spectra of metalloporphyrins. In the spectra of the β-octaalkylporphyrins **3a**–**w**, the γ(NH) and δ(NH) vibrations are observed in the regions of 690–710 and 960–990 cm^{-1}, respectively (see Table 5).The positions of the bands change only slightly upon *meso*-substitution. No relationship between the effects of the substituents (OMe or NO_2) in the benzene rings of the porphyrins **3i**–**m**,**o**–**s** and the NH deformation vibration frequencies was revealed.

The NH stretching vibrations of porphyrins are characteristic and their identification presents no problems. The ν(NH) frequency of porphyrins is ~190 cm^{-1} lower than that of pyrrole because the electron density is transferred from the pyrrole fragments to the macrocyclic aromatic π system, the lowering of the ν(NH) vibration frequency being accompanied by stabilisation of the porphyrin anion. Further lowering of the stretching vibration frequency (by ~15 cm^{-1}) and stabilisation of the porphyrin anion (*i.e.*, an increase of the acid ionisation constant) occur as the aromaticity increases in the porphyrin–tetraazaporphyrin–phthalocyanine series (Table 7).

Table 7. Frequencies of NH symmetrical stretching vibrations and the first-stage acid ionisation constants (K_1) for porphyrins in DMSO solutions.[7]

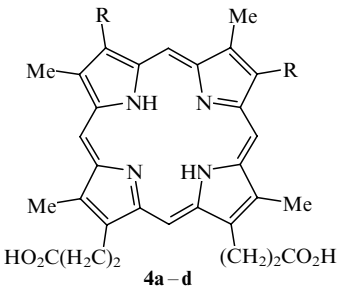
Porphyrin	ν(NH) /cm^{-1}	pK_1
Porphin	3305	22.35 ± 0.02
Octamethylporphyrin	3311	–
meso-Tetraphenylporphyrin	3315	21.15 ± 0.03
Tetrabenzoporphyrin	3305	18.53 ± 0.05
Tetraazaporphyrin	3300	12.36 ± 0.18
Phthalocyanine	3290	10.73 ± 0.03
Mesoporphyrin	3315	–
Deuteroporphyrin	–	25.30 ± 0.04

The ν(NH) frequency becomes higher on both deep alkylation and hydrogenation of porphyrins due to an increase of the electron density on the nitrogen atoms. The ν(NH) vibration band in the spectrum of the octaalkylporphyrin **3t** is shifted to the high-frequency region by ~ 30 cm^{-1} compared to that in the spectrum of porphyrin. This effect is further enhanced (by ~ 10 cm^{-1}) in the presence of the electron-donating alkyl substituents ($CH_3-C_6H_{13}$ or $C_{11}H_{23}$) at the *meso* positions of the macrocycle. At the same time, the introduction of aryl substituents at the *meso* positions leads to the low-frequency shift (by ~ 15 cm^{-1}) of the ν(NH) vibration bands compared to the analogous band observed in the spectrum of the porphyrin **3t** (see Table 5).

4. Metalloporphyrins

The molecular symmetry of metalloporphyrins is higher than that of porphyrins due to the replacement of two hydrogen atoms in the coordination centre of the porphyrin ligand by the metal atom and equalisation of the geometric parameters of the pyrrole fragments in metal complexes. Changes in the geometric parameters of the porphyrin molecule upon complex formation are clearly manifested in the IR spectra. Thus, the number of absorption bands decreases and their symmetry and resolution increase. These facts are associated with degeneration of the energies of particular types of vibrations as the molecular symmetry becomes higher.[2, 31–33]

In the spectra of metalloporphyrins, the following NH absorption bands disappear first: the NH stretching vibration bands in the region of 3345–3360 cm^{-1} and the NH deformation vibration bands in the regions of 720–740 and 960–980 cm^{-1}.[2, 7] In the spectra of mesoporphyrin **4a**, protoporphyrin **4b**, deuteroporphyrin **4c** and hematoporphyrin **4d**, the fingerprint region where the skeletal vibrations of the porphyrin molecule are located is most sensitive to the introduction of the metal atom.[34]



4a–d

R = Et (**a**), CH=CH$_2$ (**b**), H (**c**), CH(Me)OH (**d**).

The formation of metalloporphyrin from porphyrin leads to sharp changes in the intensities of the bands in the regions of 675–683 (I) and 705–711 cm^{-1} (II). A substantial decrease in the intensity of the band I is accompanied by an increase in the intensity of the band II. The positions of these bands depend only slightly on the nature of the metal atom. Other skeletal vibrations of the pyrrole rings of porphyrin are less sensitive to the introduction of the metal atom into the coordination centre of the molecule.

All absorption bands caused by vibrations of the peripheral substituents of porphyrin are weakly sensitive to the introduction of the metal atom. Thus, the intense band at 900 cm^{-1} observed in the spectrum of the protoporphyrin **4b** is retained on complex formation with divalent metals. On going to the porphyrin complex with Mn(III), the relative intensity of this band decreases, but its position remains unchanged. Analogous situations are observed for the complexes of the mesoporphyrin **4a** and the hematoporphyrin **4d**.[34] The presence of at least two free β positions in the pyrrole rings of porphyrin leads to substantial changes in the spectral pattern. Thus, the number of the bands in the region of 900–1000 cm^{-1} in the spectra of complexes of the deuteroporphyrin **4c** is smaller and their intensities are higher compared to those observed in the spectrum of the ligand.

The changes in the IR spectra of porphyrins on complex formation with divalent metals depend on the nature of the metal atom (Tables 8 and 9). However, the most substantial changes in the spectral characteristics of the porphyrin complexes are observed in the case of polyvalent metal ions. The formation of these complexes results in essential changes in the structure and symmetry of the metalloporphyrin molecule due to the displacement of the cation from the plane of the macrocycle.[7, 35]

In the case of *meso*-tetraphenylporphyrin complexes, the most essential changes associated with complex formation are observed in the region of the spectrum where the out-of-plane γ(CH) deformation vibrations of the pyrrole ring are manifested (~ 800 cm^{-1}).[25] The IR spectrum of *meso*-tetraphenylporphyrin has three bands in this region (at 783, 797 and 810 cm^{-1}), the intensities of the first and third bands being equal and low. The band at 797 cm^{-1} is the most intense one. In the spectrum of the corresponding metalloporphyrin, the band at 783 cm^{-1} disappears, the intensity of the band at 810 cm^{-1} decreases sharply and the latter is shifted to the high-frequency region due, apparently,

Table 8. Positions of absorption maxima (cm^{-1}) in the IR spectra of the porphyrin complexes **4a–d**.[7, 34]

Compound **4**	Complexes with				
	Zn	Cu	Co	Pd	Mn[a]
a	831	832	832	834	839
	896	897	897	898	898
	950	951	951	952	958
	982	980	985	987	989
	1193	1194	1194	1194	1195
	1435	1433	1432	1433	1434
b	835	833	834	835	838
	900	898	902	902	917
	947	948	948	950	958
	984	987	990	992	993
	1193	1196	1200	1200	1200
	1434	1433	1435	1434	1435
c	833	833	833	834	850
	898	989	898	900	920
	950	952	952	954	956
	981	984	983	984	989
	1200	1200	1200	1200	1205
	1434	1437	1437	1438	1437
d	834	832	832	834	837
	928	920	928	832	930
	952	952	954	956	955
	982	982	984	985	990
	1193	1002	1203	1208	1210
	1433	1433	1433	1432	1433

[a] Porphyrin–Mn(Cl) complexes.

Table 9. Positions of absorption maxima (cm^{-1}) in the IR spectra of *meso*-tetraaryl-substituted porphyrin complexes.[20,25]

Substituent in the benzene ring	Complexes with				
	Zn	Ni	Co	Cu	Mg
H	737	752	740	745	735
	802	809	802	797	800
	971	980	974	977	982
	1070	1079	1073	1070	1075
	1171	1166	1176	1173	1164
2-OMe	742	758	747	751	740
	805	808	803	798	801
	994	1007	996	1000	1004
	1050	1050	1051	1049	1055
	1182	1184	1181	1179	1183
3-OMe	771	785	776	781	774
	806	810	808	803	800
	847	864	852	860	855
	1005	1009	1005	1003	1002
	1076	1092	1084	1080	1079
	1172	1155	1165	1162	1166
4-OMe	794	811	800	804	792
	850	854	844	840	853
	990	1001	993	998	995
	1110	1107	1109	1107	1109
	1174	1186	1178	1174	1174
2-Me	740	752	743	747	738
	811	816	809	804	810
	993	999	995	998	990
	1055	1067	1054	1051	1056
	1182	1176	1183	1181	1188
3-Me	770	784	773	776	768
	892	899	890	885	890
	790	792	792	799	789
	1001	1005	1001	1003	1000
	1107	1107	1100	1092	1083
	1155	1186	1153	1151	1164
4-Me	787	804	792	796	789
	854	859	852	847	852
	996	1007	999	1003	1001
	992	998	996	999	990
	1110	1090	1112	1108	1109
	1188	1175	1183	1180	1174

to the fact that complex formation leads to lowering of the electron density in the macrocycle.

The high-frequency shift of the band at 797 cm^{-1} is observed in the spectra of porphyrin complexes with polyvalent metal ions. In the case of Mo(V) and W(V), this band is observed at 805 cm^{-1}.[36] Apparently, the shift of the band at 797 cm^{-1} in the spectra of complexes with polyvalent ions is associated with the geometric characteristics of these complexes in which the metal ion deviates substantially from the plane of the molecule. The noncoplanar arrangement of the metal atom reduces the possibility of transfer of the σ- and π-electron density from the nitrogen atom to the metal atom as a result of which the complexes should be destabilised.

Complex formation causes substantial changes in the frequencies and intensities of the bands in the region of 964–1030 cm^{-1} where the in-plane δ(CH) deformation vibrations of the pyrrole fragments of the porphyrin molecule are manifested. It is worthy of note that the intensity of the band at 1003 cm^{-1} in the spectrum of *meso*-tetraphenylporphyrin rises sharply upon complex formation. Koifman[34] believed that this band is associated with two types of vibrations of the pyrrole fragments, *viz*., with in-plane δ(CH) deformation vibrations and ν[C(β)–C(β)] stretching vibrations. As mentioned above, the introduction of electron-withdrawing substituents into the pyrrole ring results in a more substantial change in the dipole moment of the molecule in the course of vibration. This leads to significant changes (generally, to a rise) in the intensities of the out-of-plane and in-plane CH deformation vibration bands. By analogy, the increase in the intensity of the band at 1003 cm^{-1} in the spectrum of *meso*-tetraphenylporphyrin can be related to the electron density redistribution in the molecule upon complex formation. Apparently, the δ(CH) vibrations make the major contribution to this absorption band.

Complex formation with *meso*-tetraaryl-substituted porphyrins as well as the change of the metal atom lead to substantial changes in the region of 690–758 cm^{-1} (see Table 9) in which two out-of-plane deformation vibration bands of the aryl groups are observed. The position of one band depends on the nature of the metal atom and changes from 690 to 708 cm^{-1}.[20,25] The second band belongs to the most intense bands manifested in the IR spectra of metal complexes and is observed in the region of 732–758 cm^{-1}. The frequencies and intensities of the ν(C–C) stretching vibration bands of the benzene rings are also changed substantially upon complex formation. Thus, two intense bands appear instead of three medium intensity bands in the region of 1430–1590 cm^{-1}. It was noted[37] that the changes in the electronic structure of the *p* and *d* shells of the metal atom as well as the changes in the geometric parameters of the coordination centre caused by complex formation have no effect on the position and intensity of the ν(C–C) band (1590 cm^{-1}) in the spectrum of *meso*-tetraphenylporphyrin. Hence, there is no clear correlation between the electronic structure of the coordination centre and the ν(C–C) vibration frequency. However, it can be stated that the C–H and C–C vibrations of the benzene rings depend on the change in the symmetry of the π system of the macrocycle due to complex formation.

The spectral characteristics of the complexes of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**3t**) and its *meso*-di-(**3a**–**c**,**g**–**m**) and -tetrasubstituted derivatives (**3u**,**w**) with Zn, Cu and Ni[38] are given in Table 10. Complex formation leads to the disappearance of the NH vibration bands in the IR spectra and to a decrease in the number of the bands in the regions where C–C vibrations of the pyrrole and benzene rings are manifested. In the case of both protoporphyrin and deuteroporphyrin, the spectral characteristics are less affected by the introduction of the metal ion into the coordination centre of the porphyrin molecule. However, the changes are comparable with those observed on coordination of *meso*-tetraphenylporphyrin.

The region about ~1000 cm^{-1} in which the metal-sensitive bands are most pronounced is of particular interest. The spectra of all complexes have three bands at ~980, 955 and 910 cm^{-1}, the positions of the first and third bands being dependent on the nature of metal.[27,38] The high-frequency shifts of these bands increase in the series Zn < Cu < Ni. It should be noted that the above-mentioned sequence corresponds to the hypsochromic shifts of the absorption bands in the electronic absorption spectra of the complexes of **3a**–**c**,**g**–**m**,**t**,**u**,**w** (see Table 10).[39] The bands at 955 and 910 cm^{-1} in the IR spectrum of the copper complex of octaethylporphyrin belong to deformation vibrations of the alkyl groups, which is confirmed by the absence of these bands in the spectrum of the copper complex of porphyrin.[34] The band at 980 cm^{-1} may be assigned to deformation vibrations of the porphyrin ring. An analogous assignment was made for the copper complex of octaethylporphyrin.[25]

The CH vibration frequencies of the methine bridges in the *meso*-unsubstituted (**3t**) and the *meso*-disubstituted β-octaalkylporphyrins (**3a**–**s**) depend substantially on the nature of the metal ion.[27] These frequencies at 3110, 1220 and 835 cm^{-1} belong to stretching and deformation (in-plane and out-of-plane) CH vibrations, respectively. The positions of the absorption maxima of the CH deformation vibrations of the methine bridges in porphyrins are given in Table 10. The stronger the coordination of the metal atom and the higher its electronegativity, the larger the high-frequency shift. The in-plane deformation vibrations depend on

Table 10. Positions of absorption maxima in the IR (cm^{-1}) and electronic absorption (nm) spectra of the β-octaalkylporphyrin complexes **3a–c,g–m,t,u,w**.[38,39]

Compound **3**	ν [a] for complexes with			$\lambda_{max}(\log\varepsilon)$ [b] for complexes with			Compound **3**	ν [a] for complexes with			$\lambda_{max}(\log\varepsilon)$ [b] for complexes with		
	Zn	Cu	Ni	Zn	Cu	Ni		Zn	Cu	Ni	Zn	Cu	Ni
a	834	835	836	570(3.66)	568(3.58)	556(3.42)	**k**	839	840	841	574(3.86)	570(3.90)	569(3.82)
	917	925	929	537(3.78)	534(3.74)	526(3.18)		912	920	924	540(4.29)	538(4.19)	535(4.26)
	977	982	989	409(4.63)	408(4.56)	398(4.17)		986	994	999	413(5.31)	410(5.17)	408(5.20)
	1217	1220	1226					1226	1228	1232			
b	836	837	838	570(3.65)	568(3.60)	510(3.45)	**l**	840	842	843	574(3.78)	572(3.70)	568(3.81)
	918	924	927	538(3.78)	535(3.42)	526(3.15)		907	912	921	541(4.30)	539(4.25)	536(4.20)
	982	987	992	409(4.62)	408(4.48)	398(4.20)		982	988	911	413(5.27)	410(5.20)	406(5.31)
	1231	1236	1239					1207	1214	1219			
c	835	836	837	572(3.64)	568(3.62)	558(3.38)	**m**	846	846	847	574(3.59)	570(3.59)	567(3.72)
	918	925	929	538(3.74)	536(3.42)	526(3.19)		918	924	928	540(4.17)	538(4.09)	536(4.01)
	982	988	994	410(4.61)	409(4.50)	398(4.18)		985	990	996	414(5.34)	412(5.41)	410(5.39)
	1233	1238	1242					1234	1240	1244			
g	836	836	838	572(3.60)	569(3.64)	558(3.40)	**t**	834	835	836	569(3.95)	569(3.86)	557(3.91)
	922	926	932	539(3.75)	535(3.50)	525(3.19)		911	918	922	538(3.62)	534(3.54)	526(3.60)
	984	987	995	411(4.58)	409(4.50)	397(4.19)		986	991	997	403(5.21)	399(5.17)	396(5.14)
	1234	1239	1246					1228	1231	1237			
h	836	837	838	575(3.99)	573(3.87)	570(3.79)	**u**	838	838	839	578(3.67)	576(3.60)	572(3.60)
	912	919	923	541(4.26)	539(4.31)	536(4.28)		912	917	920	544(3.82)	542(3.80)	539(3.84)
	980	985	992	412(5.01)	410(5.08)	408(5.13)		988	992	997	420(4.91)	418(4.90)	414(4.89)
	1220	1223	1229					1223	1227	1234			
i	840	842	843	573(3.96)	571(3.91)	569(3.90)	**w**	837	837	839	582(3.62)	580(3.69)	578(3.60)
	916	923	925	540(4.26)	538(4.31)	536(4.40)		915	920	924	547(3.80)	544(3.78)	542(3.81)
	980	986	992	411(5.08)	409(5.11)	406(5.21)		986	990	995	422(4.92)	420(4.94)	416(4.89)
	1222	1225	1231					1225	1228	1233			
j	838	839	840	574(3.87)	571(3.80)	5.68(3.92)							
	910	916	920	540(4.30)	537(4.38)	535(4.36)							
	988	994	998	413(5.20)	411(5.13)	409(5.27)							
	1209	1215	1220										

[a] In KBr pellets; [b] a solution in chloroform.

the nature of the metal atom more strongly than the out-of-plane vibrations. The regularity revealed for the δ(CH) and γ(CH) vibrations of the methine bridges agrees with the changes that occur at 1000 cm^{-1} in the IR spectra upon complex formation and is confirmed by the results of studies by electronic absorption spectroscopy.

Therefore, examination of the IR spectra demonstrated that the introduction of the metal ion into the porphyrin molecule affects substantially the macrocycle (particularly, its π-electron system) and causes changes in the frequencies and intensities of vibrations of most of the bonds and molecular fragments.

III. ^{1}H NMR spectra of porphyrins and their precursors

Studies performed in the last decades demonstrated that ^{1}H NMR spectra are very informative and adequately reflect the structural features of porphyrins.[40–59] The presence of the extended delocalised π-electron system of the porphyrin macrocycle gives rise to a strong ring current in the molecules placed in the magnetic field. The ring current causes anisotropic shielding of the protons located in the field of its action and (together with the diamagnetic component of paired σ-electrons) leads to a substantial shift of their signals in the ^{1}H NMR spectra. It can be stated that the ring current and aromaticity of porphyrins change in a similar way in response to the analogous changes in the molecular structure of the porphyrin and the medium, which is most clearly seen on comparison of the spectra of porphyrins and their precursors.

1. Pyrroles

The chemical shifts of protons depend on the electron density on the hydrogen atom, the ring current of the molecule, the π-electron charge on the atom bound to the proton under consideration and the steric effects resulting from interactions with the substituents or the heteroatoms involved in the ring. Generally, separation of these effects presents a considerable problem.

The introduction of substituents into the pyrrole molecule leads to essential spectral changes.[9,10,13] A comparison of the characteristics of pyrrole (**1a**) and 3,4-dimethylpyrrole (**1m**) (Table 11) demonstrated that the positions of the signals for the protons of the CH groups of the pyrrole rings remain unchanged. Apparently, the β-substitution in the pyrrole ring exerts only a slight effect on the π-electron system of the molecule. In the spectrum of 2,3,4-trimethylpyrrole (**1o**), the signals for α-H are shifted upfield by 1.06 ppm compared to those in the spectrum of unsubstituted pyrrole due, apparently, to the positive inductive effect of the methyl group. Correspondingly, the downfield shift of the signal for α-H (0.43 ppm) observed on going from 3,4-dimethylpyrrole (**1m**) to 2-ethoxycarbonyl-3-ethyl-4-methylpyrrole (**1q**) occurs due to the effect of the electron-withdrawing ester group.

The most essential changes associated with chemical modifications of the molecule are observed in the region of the signals for the protons of the β-methyl and NH groups (see Table 11). An increase in the number of methyl groups in the pyrrole ring on going from the compound **1m** to the compound **1o** causes upfield shifts of the signals for the protons of the alkyl substituents by 0.13 ppm. The introduction of the electron-withdrawing ester or formyl group into the molecule results in downfield shifts of these signals by ~0.2 ppm. Of all the structures under consideration,

Table 11. Positions and multiplicities of the signals in the ^{1}H NMR spectra of pyrrole (**1a**) and its derivatives **1b**–**s**, **5a**,**b**.[9, 10, 12]

Compound	δ(NH)	δ(β-CH_3)	δ(β-Alk)	δ(α substituent)		δ(OCH_2CH_3)	
				H	another substituent	CH_3	CH_2
1a	7.62 s (1H)	–	–	6.18 s (2H)	–	–	–
1b	9.00 s (1H)	2.08 s (3H)	1.75 s (3H)	–	2.02 s	1.30 t	4.16 q
1c	9.68 s (1H)	2.24 s (3H)	1.17 t (3H), 2.45 q (2H)	–	2.59 s	1.38 t	4.35 q
1d	8.62 s	2.20 s	0.95 t, 1.28 m, 1.82 m, 2.28 t	–	2.13 s	1.28 t	4.23 q
1e	8.84 s	2.21 s	0.84 t, 1.30 m, 1.82 m, 2.27 t	–	2.09 s	7.27 [a] m	5.22 m
1f	8.80 s	2.23 s	0.89 t, 2.41 q	–	2.01 s	7.25 [a] m	5.19 m
1g	8.75 s	2.24 s	0.84 t, 2.69 q	–	–	7.30 [a] m, 1.33 t	4.32 m
1h	9.88 s	2.54 s	0.87 t, 2.69 q	–	12.60 s	1.32 t	4.31 q
1i	10.05 s	2.53 s	0.88 t, 2.71 q	–	12.64 s	1.33 t	4.30 q
1j	8.88 s	2.20 s	0.85 t, 2.71 q	–	–	1.26 t	4.24 q
1k	9.01 s	2.18 s	0.84 t, 2.74 q	–	–	1.27 t	4.23 q
1l	9.82 s (1H)	2.22 s (3H)	0.87 t, 1.87 m, 1.29 m, 2.65 t	6.20 s (1H)	–	1.32 t	4.31 q
1m	7.17 s (1H)	2.01 s (6H)	–	6.18 s (2H)	–	–	–
1n	6.97 s (1H)	1.50 s (2H) [b]	–	–	5.11 s (6H)	–	–
1o	6.72 s (1H)	2.02 s (6H)	–	6.02 s (1H)	5.12 s (3H)	–	–
1p	6.99 s (1H)	1.86 s (3H)	1.05 t (3H), 2.37 q (2H)	5.09 s (1H)	–	–	–
1q	9.88 s (1H)	2.24 s (3H)	1.14 t (3H), 2,40 q (2H)	6.61 s (1H)	–	1.32 t	4.27 q
1r	10.87 s	2.27 s	1.05 t, 2.36 q	–	9.45 s	–	–
1s	10.09 s	2.24 s (3H)	1.21 t (3H), 2.74 q (2H)	–	6.89 s (3H), 9.58 s (1H)	–	–
5a	9.73 s	2.22 s	1.08–1.58 m, 2.18–2.44 m	–	2.14 s	1.31 t	4.25 q
5b	9.84 s	2.27 s	1.26 m, 2.27–2.48 m	–	9.54 s	–	–

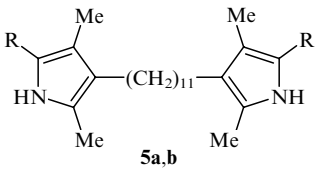
Note. Hereinafter, the ^{1}H NMR spectra were measured in $CDCl_3$; the chemical shifts (δ) are given in ppm. [a] Signals for the protons of the phenyl groups; [b] signals for β-H.

this chemical shift is maximum (~0.5 ppm) in the case of the carboxy derivatives.

The chemical shifts of the signals for the protons of the NH groups are changed more substantially. Methylation of the pyrrole ring (the compounds **1a** and **1o**) is accompanied by the upfield shifts of these signals by ~0.9 ppm (see Table 11). The signals for the protons of the NH groups are shifted downfield (up to 3.3 ppm) upon introduction of electron-withdrawing groups at the α positions of pyrroles.

The spectral characteristics (the intensities and multiplicities of the signals) agree well with the structures of the pyrroles synthesised. The signals for the protons of the ester (at δ 1.2–4.5) and carboxy (at δ 9.45–12.65) groups remain very characteristic and do not overlap with the signals of other proton-containing groups.

No substantial changes in the chemical shifts of the signals for the protons of the β-alkyl substituents and functional groups are observed on going from the compounds **1c**,**q** to β-bound pyrroles **5a**,**b**.



5a,**b**

R = CO_2Et (**a**), CHO (**b**).

In the ^{1}H NMR spectra of the compounds **5a**,**b**, the arrangement of the signals of the $(CH_2)_{11}$ methylene bridge linking the β positions of the pyrrole fragments is of interest.[60] The signals for the protons of two methylene groups directly bound to the pyrrole ring (see Table 11) are resolved from the signals for the protons of the remaining nine units of the bridge. The intensity distribution of the signals provides information on the relative number of equivalent protons (4 and 18, respectively). The signals for the protons of the NH groups in the spectrum of the compound **5b** are shifted upfield and are broadened compared to those observed in the spectrum of the pyrrole **1r**. Since the bispyrroles **5a**,**b** consist of two pyrrole rings separated from each other, the observed changes are, apparently, associated with the fact that solutions contain several conformers with different relative arrangements of the pyrrole nuclei. As a result, the positions of the NH groups in the bispyrrole molecule are nonequivalent (different shielding of the nuclei in different molecules or in different positions of a single molecule). On the contrary, the signals for the protons of the NH groups in the spectra of analogous dipyrrolylmethenes and biladienes are shifted downfield due to extension of the conjugated system and enhancement of the aromaticity of the pyrrole rings.[61]

2. Dipyrrolylmethanes

A comparison of the ^{1}H NMR spectra of the compounds **1b** and **2a** revealed no substantial changes in the region of the signals for the protons of the NH groups [12, 13] (Tables 11 and 12) due, apparently, to the absence of conjugation between the nearby π-electron systems of the pyrrole rings. On going from unsubstituted dipyrrolylmethane to the carboxy derivatives, the signals for the protons of the NH groups are shifted downfield (by ~0.5 ppm) due, presumably, to the electron-withdrawing effect of the carboxy groups. Methylation at the β positions of dipyrrolylmethane is accompanied by slight upfield shifts of the signals for the protons of the NH groups. The shifts successively increase on going from β-dialkyl-substituted dipyrrolylmethane to the β-tetraalkyl-substituted analogue and as the length of the alkyl substituent increases (the compounds **2a**,**c**,**d**), which is consistent with the positive inductive effect of the alkyl substituents.

The introduction of the phenyl substituent at the *meso* position of dipyrrolylmethane (the compound **2k**) leads to a slight downfield shift of the signal for the protons of the NH groups by 0.2 ppm compared to that in the spectrum of unsubstituted dipyrrolylmethane. A more substantial shift is observed in the spectrum of the structural isomer **2l**. Apparently, the above-considered changes can be attributed to the small negative inductive effect of the phenyl groups.

Chemical modifications at positions 5 and 5′ in the dipyrrolylmethane molecule (on going from the ethoxycarbonyl derivatives to the carboxy analogues) have virtually no effect on the positions of the signals for the β-alkyl protons. However, it should be noted

Table 12. Positions and multiplicities of the signals in the ^{1}H NMR spectra of dipyrrolylmethanes and their derivatives.[12–14]

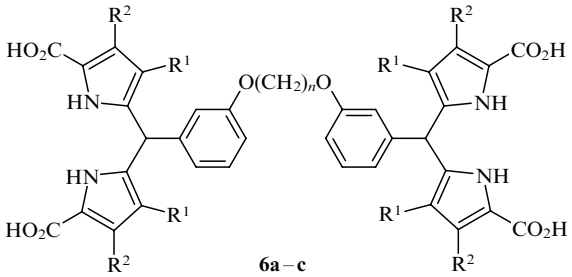
Compound	δ(NH)	δ(β-CH_3)	δ(*meso*-H)	δ(Alk)	δ(Ar)
2a	9.24 s (2H)	2.92 s (6H)	3.87 s (2H)	1.87 s (6H)	–
2b	9.55 s (2H)	2.94 s (6H)	5.30 s (2H)	0.82 t (6H), 1.25 m (4H), 1.85 m (4H), 2.30 t (4H)	–
2c	9.14 s (2H)	2.97 s (6H)	3.73 s (2H)	0.98 t (6H), 2.30 q (4H)	–
2d	9.10 s (2H)	2.91 s (6H)	3.80 s (2H)	0.84 t (6H), 1.25 m (4H), 1.86 m (4H), 2.31 t (4H)	–
2f	9.20 s (2H)	2.94 s (6H)	3.78 s (2H)	6.49 s (2H)	–
2h	9.75 s (2H)	2.21 s (6H)	5.81 s (1H)	0.80 t (6H), 1.21 m (4H), 1.87 m (4H), 2.23 t (4H)	6.68 m (3H; 3,4-H), 6.90 d (2H; 2-H)
2i	9.69 s (2H)	2.22 s (6H)	5.89 s (1H)	0.79 t (6H), 1.22 m (4H), 1.90 m (4H), 2.25 t (4H)	6.61 m (3H; 3,4-H), 6.90 d (2H; 2-H)
2j	9.81 s (2H)	2.16 s (6H)	4.84 s (1H)	0.94 t (6H), 1.20 m (4H), 1.92 m (4H), 2.34 t (4H)	6.65 m (3H; 3,4-H), 6.90 d (2H; 2-H)
2k	9.32 s (2H)	2.22 s (6H)	4.01 s (1H)	0.81 t (6H), 1.19 m (4H), 1.87 t (4H), 2.28 t (4H)	6.60 m (3H; 3,4-H), 6.90 d (2H; 2-H)
2l	9.52 s (2H)	2.23 s (6H)	4.12 s (1H)	0.83 t (6H), 1.20 m (4H), 1.85 m (4H), 2.32 t (4H)	6.69 m (3H; 3,4-H), 6.90 d (2H; 2-H)
2n	9.69 s (2H)	2.20 s (6H)	5.88 s (1H)	0.81 t (6H), 1.19 m (4H), 1.89 m (4H), 2.28 t (4H)	6.70 d (2H; 3-H), 6.92 d (2H; 2-H), 3.66 s (3H; CH_3)
2p	9.48 s (2H)	2.22 s (6H)	5.31 s (1H)	0.82 t (6H), 1.21 m (4H), 1.84 m (4H), 2.34 t (4H)	6.72 m (2H; 3,4-H), 6.92 d (2H; 2-H), 3.68 s (3H; CH_3)
2r	9.52 s (2H)	2.20 s (6H)	5.89 s (1H)	0.84 t (6H), 1.20 m (4H), 1.79 m (4H), 2.34 t (4H)	6.74 m (3H; 3,4-H), 6.96 d (1H; 2-H), 3.70 s (3H; CH_3)
2t	9.54 s (2H)	2.24 s (6H)	5.83 s (1H)	0.80 t (6H), 1.24 m (4H), 1.80 m (4H), 2.36 t (4H)	6.68 d (2H; 3-H), 6.90 d (2H; 2-H)
2v	9.56 s (2H)	2.27 s (6H)	5.81 s (1H)	0.83 t (6H), 1.19 m (4H), 1.82 m (4H), 2.36 t (4H)	6.74 m (2H; 3,4-H), 6.98 d (2H; 2-H)
2x [a]	7.81 s (2H)	–	3.80 s (2H)	1.82 s (6H)	–
6a	9.07 s (4H)	2.17 s (12H)	5.44 s (2H)	0.86 t (12H), 2.29 q (8H)	6.95 t (4H; 3,4-H), 7.13 m (4H; 2-H), 4.12 m (2H; CH_2), 3.54 t (4H; CCH_2)
6b	9.62 s (4H)	2.19 s (12H)	5.36 s (2H)	0.84 t (12H), 2.31 q (8H)	7.03 m (4H; 3,4-H), 7.28 m (4H; 2-H), 4.10 m (4H; CH_2), 3.78 t (4H; CCH_2)
6c	9.20 s (4H)	2.21 s (12H)	5.28 s (2H)	0.82 t (12H), 2.30 q (8H)	7.14 m (4H; 3,4-H), 7.31 m (4H; 2-H), 4.12 m (4H; 2-CH_2), 3.84 t (4H; OCH_2)

[a] According to the published data.[30]

that the introduction of the phenyl substituent at the *meso* position of the molecule is accompanied by the upfield shifts (by ~0.7 ppm) of the signals for the protons of the methyl substituents at positions 3 and 3′ (see Table 12) due to the shielding effect of the ring current of the phenyl substituent.

In the ^{1}H NMR spectra of the 5,5′-diesters **2a**,**c**,**d**,**f**,**k**,**l**, the signals for the *meso*-protons are observed as a pronounced singlet in the region δ 3.73–4.12. As expected, the signals are shifted downfield (by ~2 ppm) on going to the 5,5′-dicarboxy derivatives **2b**,**h**,**i**,**n**,**p**,**r**, (see Table 12). The electron-withdrawing effect of the carboxy group is identical in both the *meso*-unsubstituted and *meso*-aryl-substituted dipyrrolylmethanes. The introduction of the phenyl substituent at the *meso* position of porphyrin leads to an increase in the downfield shift (by ~0.5 ppm) in the case of both the ethoxycarbonyl and carboxy derivatives. Apparently, this fact can be explained by a small negative inductive effect of the substituent. The signals for the *meso*-protons and the protons of the phenyl fragments in the structural isomers **2k**,**l** are observed at δ ~4.0 and 6.6–6.9, respectively (see Table 12). In the ^{1}H NMR spectra, the signals for the protons of the unsubstituted *meso*-phenyl groups in the compounds **2h**–**l** are observed as a doublet of the *ortho*-protons and a multiplet of the *meta*- and *para*-protons. The *para*-substitution (the compounds **2n**,**t**) results in the appearance of a doublet for the *meta*-protons along with a doublet for the *ortho*-protons. In the spectra of the *meta*-substituted dipyrrolylmethanes **2p**,**v**, the signals for the *meta*- and *para*-protons again coalesce into a multiplet.

In the spectra of the linear tetrapyrrole compounds **6a**–**c**, the signals for the *meso*-protons are shifted downfield by ~1.5 ppm, whereas the positions of the signals for the protons of the β-alkyl and NH group change only slightly compared to those in the spectra of the monomeric analogue **2c**.



6a–**c**

R^1 = Me, R^2 = Et, n = 3 (**a**); R^1 = Et, R^2 = Me, n = 4 (**b**); R^1 = Me, R^2 = Et, n = 4 (**c**).

More substantial changes are observed in closed tetrapyrrole structures. It was found [61] that the signals for the protons of the β-alkyl and NH groups are shifted upfield by 0.65 and 0.28 ppm, respectively, on going from pyrrole to octamethylporphyrinogen due, apparently, to the positive inductive effect of the methyl groups at the β positions. The introduction of the methyl group at the α position of pyrrole also leads to the upfield shift of the signal for the β-alkyl protons.

3. Porphyrins

Conjugated macrocyclic structures are of most interest. The imposition of the external magnetic field on these molecules gives rise to ring currents, which make the major contribution to the observed chemical shifts. Theoretical analysis of the ^{1}H NMR spectra shows that the positions of the signals for the protons of porphyrins are determined primarily by the strength of ring π-electron currents (the macrocyclic current enclosing the molecule as a whole and local currents localised in the pyrrole nuclei). It should be noted that the macrocyclic current (Fig. 2) possesses the major 'bed' corresponding to the main 18-membered contour of conjugation and 'arms' formed by the semi-isolated C(β)–C(β) bonds in the pyrrolenine nuclei.

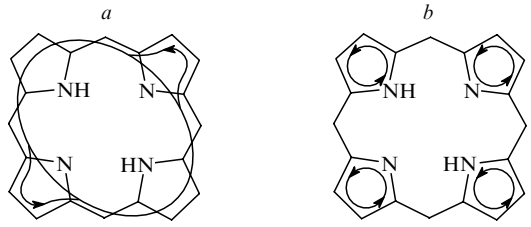


Figure 2. Schematic representation of the circuits of the ring π-electron currents in the porphyrin molecule; (*a*) the macrocyclic current, (*b*) local currents.[7, 25]

The protons at the β and *meso* positions are exocyclic with respect to the macrocyclic and local pyrrole currents and experience the deshielding influence of the latter. The signals for these protons are observed at low field (at δ from 9.7 to 11.2 for the *meso*-protons and at δ from 8.5 to 9.9 for the β-protons; see Table 13). The protons of the NH groups are exocyclic with respect to the local ring currents and endocyclic with respect to the macrocyclic current. Undoubtedly, the shielding effect of the latter prevails and the signals for the protons of the NH groups are observed at very high field (at δ from −1.4 to −4.4; see Table 13).

The β-hydrogen atoms of the pyrrole and pyrrolenine fragments are in principle nonequivalent. However, rapid (within the NMR time scale) transformations occur at room temperature and the signals for the β-protons are averaged. Two different peaks corresponding to resonance absorption of the energy by the protons of the β-CH groups of the pyrrole and pyrrolenine fragments can be observed at low temperature.[7, 62]

Table 13. Chemical shifts (ppm) of the β- and *meso*-protons and the protons of the NH groups in the ^{1}H NMR spectra of porphyrins.[7]

Porphyrin	δ(β-H)	δ(*meso*-H)	δ(NH)
Porphin	9.74	10.58	−3.76
Porphin [a]	9.92	11.22	−4.40
Octaethylporphin	–	10.18	−3.70
Ethioporphyrin-I	–	10.10	−3.67
Tetra-*iso*-butylporphyrin	9.41	–	−2.73
Tetra-n-pentylporphyrin	9.28	–	−2.75
Tetraphenylporphyrin	8.70	–	−2.81
Tetraphenylporphyrin [a]	8.45	–	−2.38
Tetra(2-methylphenyl)porphyrin	8.60	–	−2.66
Tetra(2-methoxyphenyl)porphyrin	8.65	–	−2.68
Tetra(2-bromophenyl)porphyrin	8.45	–	−2.63
Tetra(2-aminophenyl)porphyrin	8.82	–	−2.72
Tetra(3-methoxyphenyl)porphyrin	8.85	–	−2.85
Tetra(3-nitrophenyl)porphyrin	8.77	–	−2.96
Tetra(3-bromophenyl)porphyrin	8.82	–	−2.91
Tetra(3-hydroxyphenyl)porphyrin [a]	8.52	–	−2.45
Protoporphyrin	–	9.96	−4.08
Chlorin	–	9.65	−1.40
Deuteroporphyrin [a]	9.66	11.21	–

Note. In all tetrasubstituted porphyrins, the substituents are located in the *meso* positions. [a] The spectrum of a solution in CF_3CO_2H was measured.

On going from porphin to chlorin, the signals for the protons of the NH groups in the ^{1}H NMR spectra are shifted downfield, whereas the signals for the *meso*-protons are shifted upfield, *i.e.*, these signals are shifted toward each other, which is indicative of a decrease in the strength of the induced magnetic field produced by the macrocyclic ring current.[7, 62] In our opinion, two consequences of hydrogenation of one of the C(β)=C(β) bonds are responsible for these changes. First, due to hydrogenation of the C(β)=C(β) bond, the number of charge carriers providing the macrocyclic ring current is decreased by two electrons and, correspondingly, the strength of the macrocyclic ring current is diminished. Second, one of the 'arms' through which this current flows disappears, *i.e.*, the effective diameter of the ring conductor is reduced. As a result, the strength of the magnetic field induced by the macrocyclic ring current decreases.

On going from a solution of porphin (P) in deuteriochloroform to a solution in trifluoroacetic acid, the neutral form H_2P is converted into the doubly protonated form H_4P^{2+} in which the excess positive charge is located primarily on four nitrogen atoms. In this case, the electron density on the central hydrogen atoms is sharply reduced, which was confirmed by calculations for the neutral and protonated forms of porphin by the PM3 method.[63] In this connection, one would expect that the signals for the protons of the NH groups in the ^{1}H NMR spectrum will be shifted downfield upon protonation of porphin. However, the signals are shifted upfield by ~0.7 ppm (see Table 13). Simultaneously, the signals for the β- and *meso*-protons are shifted downfield. This character of the spectral changes indicates that protonation of porphin leads to a substantial increase in the strength of the magnetic field induced by the macrocyclic ring current.

Calculations [23] carried out by the PM3 method demonstrated that protonation of porphin is accompanied by a change in the geometric structure of the molecule. The C(α)–NH–C(α) fragments in the initial porphin are planar and the nitrogen atoms are sp^2-hybridised. In the protonated porphin, these fragments adopt a pyramidal structure (the nitrogen atoms have nearly sp^3 hybridisation) and the degree of involvement of the nitrogen atoms in conjugation with the α-carbon atoms is substantially reduced. This fact is confirmed by an increase in the C(α)–N bond length observed upon protonation of porphin. The above-mentioned rearrangements lead to a change in the contour of macrocyclic conjugation. In the case of protonated porphin, this conjugation is realised primarily along the outer contour of the molecule. Therefore, protonation causes an increase in the diameter of the conjugation ring resulting in upfield shifts of the signals for the internal protons and downfield shifts of the signals for the external protons.

In the case of β-alkyl substitution in porphin (on going to octaethylporphin and ethioporphyrin), the signals for the protons of the NH groups and the signals for the *meso*-protons are shifted downfield and upfield, respectively. Analogous, but more pronounced, changes are observed in the presence of a substituent in the *meso* position. It should be noted that the introduction of both electron-donating (*meso*-tetra-*iso*-butyl- and *meso*-tetra-n-pentylporphyrin) and electron-withdrawing (tetraphenylporphyrin and its derivatives) substituents gives the same results, *viz.*, the signals for β-protons and for the protons of the NH groups are shifted upfield and downfield, respectively. It seems likely that the introduction of substituents both at the β- and *meso* positions leads to reduction in the strength of the aromatic macrocyclic current regardless of the electronic nature of the substituent. The reasons for this phenomenon remain unclear.

The currents in the porphyrin molecule are substantially affected by complex formation.[7] The higher the degree of covalence of the N–H bond, the larger the decrease in the ring current due to the presence of the coordinated metal atom. Coordination to the medium-sized M^{2+} cations (M = Mg, Zn, Cd, Ni or Pd) is

accompanied by upfield shifts of the signals for the *meso*-protons (the ring current is reduced). In the spectra of the complexes in which the M^{2+} metal ion deviates from the plane due to its large radius and weak coordination interactions (M = Sn or Pb) or in the spectra of the complexes with the M^{3+} or M^{4+} ions in which the metal atom deviates from the plane of the macrocycle under the action of the extra ligands, the signals for the *meso*-protons are shifted downfield relative to those in the spectra of the porphyrin ligand. These shifts may be due to an increase in the ring current. However, this effect is insignificant and depends on the nature of the ions serving as the extra ligands.[7]

The following characteristic features should be noted in the ^{1}H NMR spectra of β-octaalkylporphyrins and their 5,15-diaryl-, 5,15-dialkyl- and 5,15-dialkyl-10,20-diaryl derivatives.[14, 19, 20, 24, 27] On going from 2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**3t**) to 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin (**3h**), the most substantial changes are observed in the region of the signals for the protons of the β-methyl and NH groups (Table 14). The upfield shifts of the

Table 14. Positions and multiplicities of the signals in the ^{1}H NMR spectra of the β-octaalkylporphyrins **3a**–**f**, **h**–**w**.[14, 19, 20, 24, 27]

Compound **3**	δ(NH)	δ(β-CH_3)	δ(*meso*-H)	δ(β-Alk)	δ(*meso*-Ar)
a	−2.11 s (2H)	3.01 s (24H)	9.82 s (2H), 4.01 s (6H)	–	–
b	−2.06 s (2H)	3.09 s (24H)	9.79 s (2H), 4.08 q (4H), 2.24 t (6H)	–	–
c	−2.04 s (2H)	3.12 s (24H)	9.77 s (2H), 4.10 t (4H), 2.20 m (4H), 1.80 t (6H)	–	–
d	−2.03 s (2H)	3.11 s (24H)	9.78 s (2H), 4.14 t (4H), 2.22 m (4H), 1.92 m (4H), 1.54 t (6H)	–	–
e	−2.07 s (2H)	3.14 s (24H)	9.80 s (2H), 4.20 t (4H), 2.25 m (4H), 1.90 m (4H), 1.50 m (4H), 1.01 t (6H)	–	–
f	−2.14 s (2H)	3.18 s (24H)	9.82 s (2H), 4.32 t (4H), 2.50 m (4H), 2.16 m (4H), 1.64 m (4H), 1.09 m (4H), 0.78 t (6H)	–	–
h	−2.42 s (2H)	2.41 s (12H)	10.17 s (2H)	3.91 t (8H), 2.11 m (8H), 1.63 m (8H), 1.03 t (12H)	7.98 d (4H; *o*-H), 7.68 m (6H; *m,p*-H)
i	−2.38 s (2H)	2.42 s (12H)	10.12 s (2H)	3.85 t (8H), 2.10 m (8H), 1.67 m (8H), 1.03 t (12H)	7.82 d (4H; *o*-H), 7.14 d (4H, *m*-H), 3.98 s (6H; CH_3)
j	−2.49 s (2H)	2.50 s (12H)	10.18 s (2H)	3.93 t (8H), 2.14 m (8H), 1.67 m (8H), 1.03 t (12H)	7.61 m (4H; *o*-H), 7.55 m (4H; *m,p*-H), 3.88 s (6H; CH_3)
k [a]	−2.38 s (2H)	2.53 s (12H)	10.19 s (2H)	3.99 t (8H), 2.18 m (8H), 1.67 m (8H), 1.09 t (12H)	7.67 d (2H; *o*-H), 7.60 t (2H; *m′*-H), 7.19 t (2H; *p*-H), 7.10 d (2H; *m*-H), 3.84 s (6H; OCH_3)
k [b]	−2.37 s (2H)	2.54 s (12H)	10.17 s (2H)	3.97 t (8H), 2.17 m (8H), 1.64 m (8H), 1.02 t (12H)	7.57–7.65 m (4H; *o, m′*-H), 7.17 t (H; *p*-H), 7.10 d (2H; *m*-H), 3.78 s (6H; OCH_3)
l	−2.49 s (2H)	2.27 s (12H)	10.20 s (2H)	3.91 t (8H), 2.07 m (8H), 1.63 m (8H), 1.10 t (12H)	8.39 d (4H; *o*-H), 7.96 d (4H; *m*-H)
m	−2.47 s (2H)	2.33 s (12H)	10.17 s (2H)	3.87 t (8H), 2.03 m (8H), 1.66 m (8H), 1.02 t (12H)	8.92 s (2H; *o*-H), 8.60 d (2H; *o′*-H), 8.24 d (2H; *p*-H), 7.77 t (2H; *m*-H)
n	−2.32 s (2H)	3.41 s (12H)	10.16 s (2H)	2.91 t (8H), 1.40 m (8H), 1.36 m (8H), 1.01 t (12H)	7.99 d (4H; *o*-H), 7.72 m (6H; *m,p*-H)
o	−2.27 s (2H)	3.99 s (12H)	10.07 s (2H)	2.79 t (8H), 2.38 m (8H), 1.50 m (8H), 1.02 t (12H)	7.87 d (4H; *o*-H), 7.70 d (4H; *m*-H), 3.99 s (6H; OCH_3)
p	−2.23 s (2H)	3.92 s (12H)	10.15 s (2H)	2.92 t (8H), 2.42 m (8H), 1.56 m (8H), 1.00 t (12H)	7.84 m (4H; *o*-H), 7.64 m (4H; *m,p*-H), 3.90 s (6H; OCH_3)
q	−2.27 s (2H)	3.98 s (12H)	10.14 s (2H)	2.90 t (8H), 2.44 m (8H), 1.52 m (8H), 1.01 t (12H)	7.91 m (2H; *o*-H), 7.66 m (6H; *m,p*-H), 3.81 s (6H; OCH_3)
r	−2.20 s (2H)	3.94 s (12H)	10.16 s (2H)	2.94 t (8H), 2.46 m (8H), 1.50 m (8H), 1.01 t (12H)	8.42 d (4H; *o*-H), 7.92 d (4H; *m*-H)
s	−2.23 s (2H)	3.92 s (12H)	10.18 s (2H)	2.87 t (8H), 2.42 m (8H), 1.48 m (8H), 1.04 t (12H)	8.76 s (2H; *o*-H), 8.54 d (2H; *o′*-H), 8.20 d (2H; *p*-H), 7.72 t (2H; *m*-H)
t	−3.80 s (2H)	3.47 s (12H)	9.91 s (4H)	3.92 t (8H), 2.19 m (8H), 1.64 m (8H), 1.11 t (12H)	–
u	–	2.42 s (24H)	4.0 q (4H), 0.65 t (6H) [c]	–	7.70 m (6H; *m,p*-H), 7.96 d (4H; *o*-H)
v	–	2.44 s (24H)	4.30 t (4H), 2.54 m (4H), 2.20 m (4H), 1.64 m (4H), 1.09 m (4H), 0.62 t (6H) [c]	–	7.78 m (6H; *m,p*-H), 7.99 d (4H; *o*-H)
w	–	2.33 s (24H)	4.50 t (4H), 2.84 m (4H), 2.20 m (4H), 1.67 m (4H) 1.01 m (4H), 0.60 t (6H) [c]	–	8.42 d (4H; *o*-H), 7.94 d (4H; *m*-H), 3.92 s (6H; CH_3)

[a] α,α-Atropoisomer; [b] α,β-atropoisomer; [c] signals for the protons of the *meso*-alkyl groups.

signals for the protons of the methyl groups (by 1.06 ppm) can be attributed to the shielding effect of the ring currents of the phenyl fragments. Apparently, the signals for the protons of the NH groups are substantially shifted downfield ($\sim$1.4 ppm) due to both the negative inductive effect of the phenyl fragments and a reduction in the strength of the macrocyclic ring current. The planar porphyrin macrocycle is deformed and its aromaticity is decreased due to steric strains caused by the phenyl groups. On going from the compound **3h** to the compound **3n**, the porphyrin macrocycle undergoes further deformation due to steric interactions between the butyl and phenyl substituents resulting in the downfield shifts (by 0.1 ppm) of the signals for the protons of the NH groups. The shielding effect of the ring currents of the phenyl fragments is manifested in the upfield shifts of the signals for the protons of the butyl substituents. These shifts are maximum (1 ppm) for the CH_2 groups directly bound to the macrocycle, whereas the positions of the signals of the terminal CH_3 groups remain virtually unchanged (0.02 ppm). The introduction of the substituents into the phenyl rings of 5,15-diphenylporphyrin (*o*,*m*,*p*-OMe or *m*,*p*-NO_2) exerts only a slight effect on the positions of the signals for the *meso* protons and for the protons of the NH groups (see Table 14).

In the ^{1}H NMR spectra of the 5,15-dialkyloctamethylporphyrins **3a**–**f**, the signals for the protons of the NH groups are shifted downfield compared to those in the spectrum of the porphyrin **3t**. Apparently, this is associated with the deformation of the molecule caused by the *meso*-substitution. The magnetic field of the π-electron ring current of the porphyrin, in turn, affects the positions of the signals for the protons of the alkyl *meso*-substituents. In this case, the spectra contain individual non-overlapping signals for the protons of the methylene and methyl fragments of the alkyl substituents. Thus, the spectrum of 5,15-dihexyl-2,3,7,8,12,13,17,18-octamethylporphyrin (**3f**) has the signal for the protons of the methylene group, which is directly bound to the macrocycle, as a triplet at δ 4.32, the signal of the adjacent methylene group as a quintet at δ 2.5 and the signals for the protons of the next two CH_2 groups as quintets at δ 2.16 and 1.64.[12] The signals of the last methylene group and the terminal methyl group are observed as a sextet at δ 1.09 and a triplet at δ 0.78.

The signals of the β-methyl groups in the spectra of the compounds **3a**–**f** are shifted downfield by $\sim$0.4–0.5 ppm compared to the corresponding signals in the spectra of 5,15-diarylporphyrins, which is attributed to elimination of the shielding effect exerted by the ring currents of the *meso*-aryl substituents.

Not only the signals for the *meso*-protons, but also the signals for the protons of the NH groups disappear in the ^{1}H NMR spectra on going from the *meso*-disubstituted porphyrins to the *meso*-tetrasubstituted compounds (**3u**–**w**). The reasons for this phenomenon remain unclear. Analogous changes are observed in the spectrum of tetraphenyl-substituted β-octamethylporphyrin.[27]

The signals for the β-methyl protons of *meso*-tetrasubstituted porphyrins are observed in the region (at $\delta \sim 2.4$) identical to that of 5,15-diarylporphyrins (see Table 14). It should be noted that the above-mentioned region is intermediate between the regions in which these signals are observed in the spectra of the octaalkylporphyrin **3t** (at δ 3.47) and its *meso*-tetraphenyl derivative (at δ 1.76),[25] which confirms the assumption that the magnetic anisotropy of the aryl *meso*-fragments exerts an effect on the protons of the β-substituents.

The chemical shifts of the protons of the phenyl fragments are observed in the region $\delta \sim 7.7-8$. The signals of the unsubstituted phenyl groups of the compounds **3h**,**n**,**u**,**v** are observed as a doublet for the *ortho*-protons and a multiplet for the *meta*- and *para*-protons. The chemical shifts of the protons of the substituted phenyl fragments vary depending on the nature of the substituent. Among the spectra of the porphyrins containing the electron-donating methoxy group in the *meso*-phenyl fragment, only the spectra of the *para*-substituted compounds **3i**,**o**,**w** have pronounced individual signals, *viz*., a doublet for the *ortho*-protons and a doublet for the *meta*-protons. In the spectra of the *meta*-methoxy-substituted compounds **3j**,**p**, the corresponding signals are observed as multiplets.

In the spectra of porphyrins containing the electron-withdrawing nitro group in the *meso*-phenyl fragment (both in the *meta*- and *para*-substituted compounds), the signals are observed as pronounced multiplets. The spectra of the *para*-nitro derivatives **3l**,**r** have a doublet for the *ortho*-protons and a doublet for the *meta*-protons. The signals of the *meta*-nitro derivatives **3m**,**s** are observed as a doublet for the *para*-protons, a triplet for the *meta*-protons and a singlet and a doublet for the nonequivalent *ortho*-protons (see Table 14).

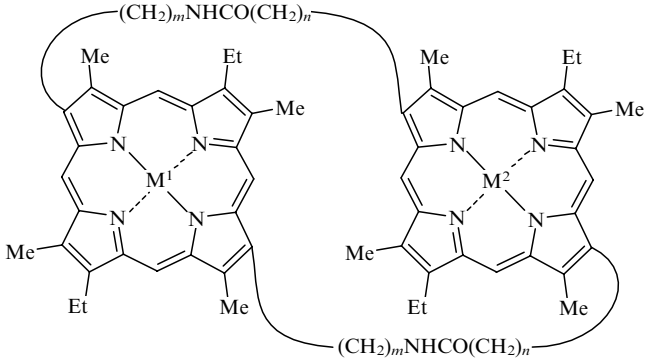
The *ortho*-methoxy-substituted porphyrin **3k** can exist as two atropoisomers (α,α and α,β), which differ by the orientation of the methoxy groups with respect to the porphyrin plane. The ^{1}H NMR spectra of these compounds are characterised by the presence of the signals for the phenyl protons as multiplets. The spectrum of the α,α-atropoisomer has two doublets for the *ortho*- and *meta*-protons and two triplets for the *meta*- and *para*-protons. The spectrum of the α,β-atropoisomer has a doublet for the *meta*-protons, a triplet for the *para*-protons and a multiplet for the *ortho*- and *meta*-protons (see Table 14).

4. Bisporphyrins

As mentioned above, the porphyrin fragments in cyclophane dimers are brought into proximity due to the bridging bonds located at the *meso* or β positions of the macrocycles. The lengths and rigidity of the bridges are responsible for the conformational flexibility of the dimer.

Interactions between the π-electron systems of the macrocycles are clearly manifested in the ^{1}H NMR spectra. The chemical shifts of the protons depend on the length of the bridge and the mutual orientation of the macrocycles.[64–86]

Dimeric porphyrins **7a**–**f** in which the porphyrin rings are linked through the β positions of the pyrrole rings by two amide bridges can exist as two isomers (*syn* and *anti*). The possibility of



7a–**n**

Compound **7**	M^1	M^2	*n*	*m*
a	H_2	H_2	0	1
b	H_2	H_2	1	1
c	H_2	H_2	0	2
d	H_2	H_2	2	1
e	H_2	H_2	1	2
f	H_2	H_2	3	1
g	Co	H_2	1	1
h	Co	Co	1	1
i	Ag	H_2	1	1
j	Ag	Ag	1	1
k	Mn	Mn	1	1
l	Mn	Co	1	1
m	Fe	Co	1	1
n	Ag	Co	1	1

formation of a particular isomer depends on the orientation of the porphyrin fragments at the instant the second amide bond is formed.[72, 73]

Figure 3 presents the ^{1}H NMR spectrum of the *anti*-isomer of the bisporphyrin **7c**, which has signals for four *meso*-protons (at δ 9.29, 8.84 and 8.78) and signals for the protons of the alkyl substituents (at δ 3.60, 3.64, 3.68 and 3.74). The signals for the protons of the NH groups are shifted upfield (δ −7.78 and −7.81) compared to those observed in the spectra of their monomeric analogues (δ −3.75). The amide bridges in the compound **7c** contain two methylene groups each. Two of these groups bound to the NH groups give a quadruplet (δ 5.8) and a doublet (δ 4.7), whereas two other groups bound to the porphyrin fragment of the dimer give signals at δ 4.1. The signals for the methylene protons of the ethyl groups are observed in the same region. The signals for the protons of the amide groups are observed as a doublet at δ 6.97. The chemical shifts of the protons of the alkyl substituents in the compound **7c** differ only slightly from those of the analogous protons in the monomeric analogue **8** (Table 15).

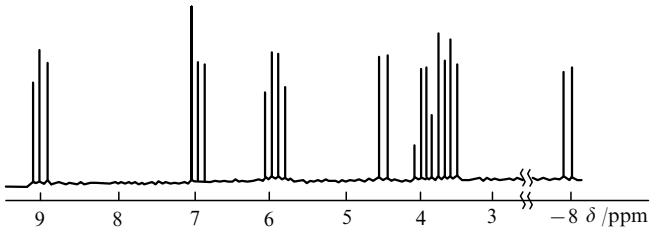
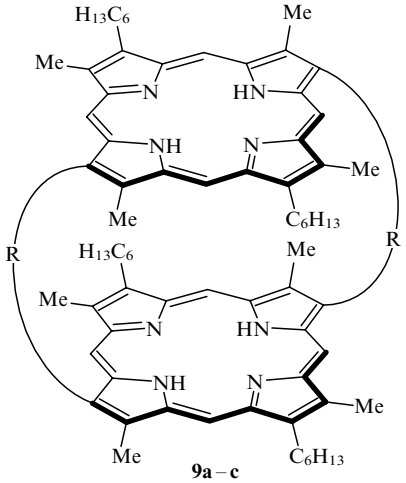


Figure 3. ^{1}H NMR spectrum of the bisporphyrin **7c** in $CDCl_3$.[73]

Three homologous dimers **9a**–**c** were investigated.[74] It was found that the porphyrin fragments approach each other by 100–120 pm as the number of the methylene groups in the bridges is decreased by one. The spectral properties are indicative of the 'face-to-face' orientation of the macrocycles.



9a–**c**

R = $(CH_2)_2CO(Bu^n)(CH_2)_3$ (**a**), $CH_2CO(Bu^n)(CH_2)_3$ (**b**), $CH_2CO(Bu^n)(CH_2)_2$ (**c**).

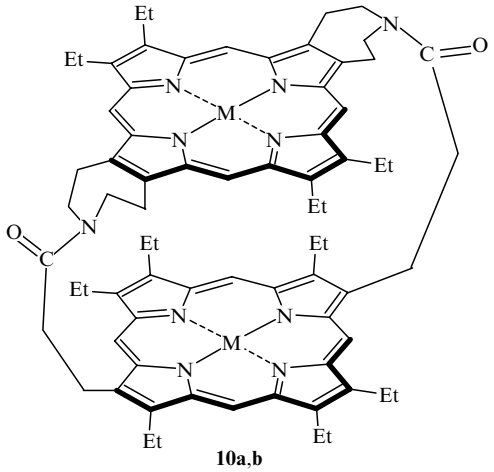
Compound **9**	*R* /pm (see [a])	δ(NH) (see [b])	λ /nm (see [c])
a	640	−6.2	383
b	540	−6.6	540
c	420	−8.5	420

[a] The distance between the porphyrin fragments; [b] in $CDCl_3$; [c] the absorption band in the electronic absorption spectrum measured in CH_2Cl_2.

Table 15. Chemical shifts (ppm) of the protons of 4,8-di(2-ethoxycarbonylethyl)-2,6-diethyl-1,3,5,7-tetramethylporphyrin (**8**) and the dimeric porphyrins **7a**–**f**.[72]

Compound	$\delta(NH_{pyrrole})$	δ(*meso*-H)	$\delta(CH_3)$
7a	−7.81, −7.93	8.90–8.98	3.65–3.90
7b	−8.14	8.70–8.91	3.58–3.60
7c	−7.78, −7.81	8.78–9.29	3.60–3.74
7d	−8.00, −7.90	8.70–8.90	–
7e	−8.30, −8.00	8.70–8.90	–
7f	−6.2	9.00–9.40	–
8	−3.75	10.10, 10.16	3.67

^{1}H NMR spectral studies revealed the existence of two conformers of dimer **10a**. In one of them, the porphyrin rings are located parallel to each other (*anti*). In another conformer, the porphyrin rings are bent with respect to each other (*syn*, 'half-open shell').[80] The conformers occur due to rigidity of the amide bonds and their appearance depends on the relative orientation of the carbonyl groups. The spectrum of a mixture of the conformers has four signals for the protons of the NH groups (at δ −8) and twelve signals for the *meso*-protons (at δ 7–10). Four signals (at δ 9) correspond to the *meso*-protons of the *anti* conformer and eight signals belong to the *meso*-protons of the *syn* conformer. The characteristic features of the crystal structure of the compound **10a** are responsible for the rather steady existence of both conformers in equal amounts. A decrease in the intensities of the signals for the protons in the spectrum of the *anti* conformer of the zinc complex of the dimer **10b** compared to the signals for the protons of the *syn* conformer indicates that the *anti* : *syn* ratio is 1 : 9. On protonation of the porphyrin **10a**, the amount of the *anti* conformer increases and the *anti* : *syn* ratio becomes equal to 1 : 6. No hypsochromic shift of the Soret band (see Section IV) is observed in the electronic absorption spectrum of the dimer **10a** compared to the spectrum of the monomeric analogue.

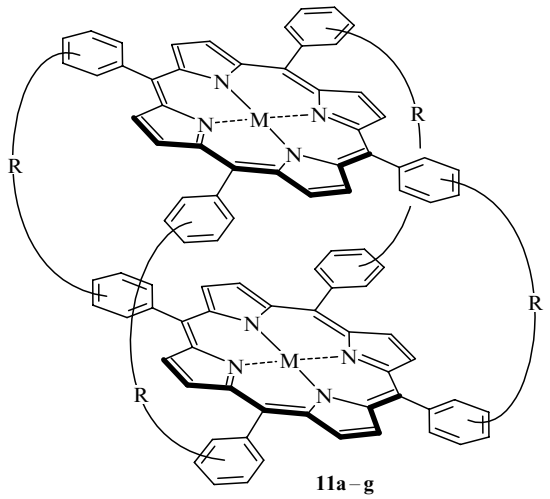


10a,**b**

M = 2H (**a**), Zn (**b**).

^{1}H NMR spectral studies established the characteristic structural features of cyclophane dimers **11a**–**d** in which the tetraphenylporphyrin fragments are linked through the *meta* or *ortho* positions of the phenyl substituents by four ether bridges.[77, 78]

The spectrum of the dimer **11a** differs from that of monomeric *meso*-tetra(3-butoxyphenyl)porphyrin in that the signals for the β-protons of the pyrrole rings are substantially split and the protons of the central CH_2 groups of the bridges give two signals. The signals for the protons of the OCH_2 and CH_2 groups are broadened. These characteristic features are retained on going from the neutral to protonated form of the dimer.



11a–g

R = *m*-O(CH$_2$)$_n$O-*m*, *n* = 4: M = H$_2$ (**a**), Zn (**b**); R = *o*-O(CH$_2$)$_n$O-*o*, *n* = 3: M = H$_2$ (**c**), Zn (**d**); R = *m*-CH$_2$NHCH$_2$-*m*, M = H$_2$ (**e**); R = *m*-CH$_2$NTsCH$_2$-*m*, M = H$_2$ (**f**); R = *m*-CH$_2$NTs-*m*, M = H$_2$ (**g**).

The cyclophane structure of the dimer imposes rigid limitations on the conformational flexibility of the O(CH$_2$)$_n$O chains. The fact that the protons of the bridging CH$_2$ groups give two signals is indicative of a skewed conformation of the ether bridges due to which the benzene rings of the adjacent macrocycles are inclined relative to each other. As a result, both fragments of tetraphenylporphyrin in the dimer adopt a nonplanar dome-shaped conformation. The resulting strain is partially relieved due to corrugation of the tetrapyrrole rings, *viz*., two opposite pyrrole fragments are bent upward, while two other fragments are bent downward. The inclination of the phenyl groups in combination with corrugation of the porphyrin macrocycle are responsible for the magnetic nonequivalence of the *ortho*-protons of the phenyl groups (external and internal) and the β-protons of the pyrrole rings. The external *ortho*-protons are located in proximity to the β-protons of the pyrrole rings directed upward, whereas the internal protons are located in proximity to the β-protons of the pyrrole rings bent downward. The distances between the pairs of the protons of the first type are smaller than those between the pairs of the protons of the second type due to which the deshielding effect of the ring currents of the macrocycle and the benzene ring in the first case is more pronounced (Table 16).

The corrugated dome-shaped conformation of the macrocycle is retained in the protonated form of the dimers. In the latter case, one pair of the protons of the NH groups is located in the centre of the macrocycle and is substantially shielded by the ring current, whereas the second pair of the protons is bent outward and the shielding effect of the ring current of the macrocycle exerted on the latter pair is weakened.

Corrugation of the porphyrin macrocycles in the protonated form of dimeric porphyrin leads to weakening of the macrocyclic ring current and strengthening of the local currents in the pyrrole fragments. For the external β-hydrogen atoms, the above-mentioned two effects compensate each other, whereas these effects with respect to the internal protons of the NH groups add up together resulting in substantial downfield shifts of the signals for these protons in the case of the dimeric porphyrin **11a** compared to its monomeric analogue (see Table 16).

The mutual effect of the macrocyclic ring currents of the adjacent porphyrin fragments leads to the nonequivalence of the protons of the NH groups in the dimer **11c**. Due to corrugation of the porphyrin rings, the distance from one pair of the protons of the NH groups to the adjacent tetrapyrrole fragment is 0.8 Å larger compared to that for the second pair.[78] This is a sufficient reason for the appearance of two signals for these protons in the ^{1}H NMR spectrum (see Table 16). The bridging groups in the dimer **11c**, unlike those in the dimer **11a**, are conformationally flexible. Judging from the fact that the positions of the signals of two OCH$_2$ groups are somewhat different (δ 4.25 and 4.11), two conformations of the bridge in solutions are rapidly (within the NMR time scale) transformed into one another. Apparently, the conformation with the unsymmetrical arrangement of the OCH$_2$ groups with respect to the tetraphenylporphyrin rings prevails.

In the ^{1}H NMR spectra of the cyclophane dimers **11e–g** in which the tetraphenylporphyrin fragments are linked through the *meta* positions of the phenyl groups by two- or three-membered bridges, the ring current exerts an even more pronounced shielding effect on the chemical shifts of the protons located below the plane of the adjacent porphyrin ring. The largest shifts are observed for the signals for the protons of the NH groups and for the *ortho*-protons of the phenyl groups because they are located between the porphyrin fragments.[79] The shifts of the signals for the β-protons of the pyrrole rings are much smaller because these protons are located at large distances from the shielding region.

Compound	δ /ppm		
	NH	phenyl *o*-H	β-H
11e	−3.78	7.81	8.43, 8.46
11f	−4.42	7.14	8.17, 8.15
11g	−4.11	7.78	8.25, 8.43
Monomer [a]	−2.81	8.25	8.86

[a] 5,10,15,20-Tetra(3-bromomethylphenyl)porphyrin.

It can be seen that the mutual effect of the porphyrin fragments is strengthened as the lengths of the bridges in the compounds **11e** and **11g** decrease. Steric restrictions resulting from the presence of the bulky substituents in the bridges of the dimer **11f** lead to rotation of the macrocycles with respect to each other about the axis passing through the centres of both porphyrin rings (in the dimers **11f** and **11e**, the angle of rotation of the macrocycles with respect to each other is 26° and 13°, respectively). The molecule adopts an energetically more favourable conformation in which the porphyrin fragments, while remaining parallel to each other, are located at shorter distances and exert a more substantial shielding effect. This fact is confirmed by the ^{1}H NMR spectral data. As in the case of the dimers **11a**,**c**, the characteristic features of the cyclophane structures of the dimers **11f**,**g** are responsible for the magnetic nonequivalence of the *ortho*-protons of the benzene rings (internal and external) and the β-protons of the pyrrole rings.

In dimeric porphyrins **12a–d**, the aromatic bridge does not provide the 'face-to-face' orientation of the macrocycles.[81] This

Table 16. Positions and multiplicities of the signals in the ^{1}H NMR spectra of the cyclophane dimers of tetraphenylporphyrin **11a**,**c** and *meso*-tetra(3-butoxyphenyl)porphyrin.[77]

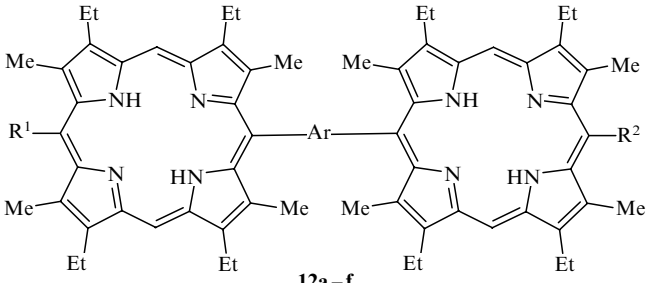
Compound	Solvent	δ(NH)	δ(β-H)	δ(H$_{bridge}$) [a]
11a	$CDCl_3$	−1.94 s	8.37 s	1.85 m (HC<u>H</u>CH$_2$O)
			9.02 s	2.27 m (<u>H</u>CHCH$_2$O)
				4.35 m (C<u>H</u>$_2$O)
	$CDCl_3$ –	−0.27 s	8.35 d	2.09 m (HC<u>H</u>CH$_2$O)
	CF_3COOH		8.51 d	2.34 m (<u>H</u>CHCH$_2$O)
				4.51 m (C<u>H</u>$_2$O)
11c	$CDCl_3$ –	−1.32 s	8.22 s	0.95 m (<u>H</u>CHCH$_2$O)
	CF_3COOH	−1.03 s	8.43 s	1.93 m (HC<u>H</u>CH$_2$O)
				4.11 t (C<u>H</u>$_2$O)
				4.25 t (C<u>H</u>$_2$O)
meso-Tetra-(3-butoxy-phenyl)por-phyrin	$CDCl_3$	−2.81 s	8.89 s	1.86 m (C<u>H</u$_2$CH$_2$O)
				4.15 t (C<u>H</u>$_2$O)

[a] The δ values are given for the underlined protons.

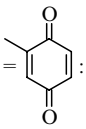
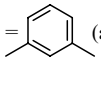
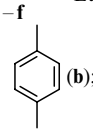
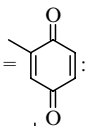
Table 17. Positions and multiplicities of the signals in the ^{1}H NMR spectra of the dimeric porphyrins **12a**–**d** and 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5-phenylporphyrin.[81]

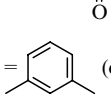
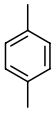
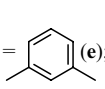
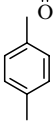
Compound	δ(NH)	δ(Ar)	δ(*meso*-H)
12a	−2.27 s (4H)	7.94 s (1H), 8.32 t (1H), 8.89 d (2H)	10.15 s (4H)
12b	−1.90 s (4H)	8.00 d (2H), 8.70 d (2H)	10.34 s (4H)
12c	−3.0 s (2H), −2.1 s (2H)	7.95 s (1H), 8.29 t (1H), 8.95 d (2H)	9.83 s (1H), 10.10 s (2H), 10.15 s (2H)
12d	−3.0 s (2H), −1.95 s (2H)	8.01 d (2H), 8.74 d (2H)	9.95 s (1H), 10.26 s (2H), 10.34 s (2H)
2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5-phenylporphyrin	−2.39 s (2H)	8.00 d (2H), 8.24 t (2H), 8.75 t (1H)	9.79 s (1H), 10.21 s (2H)

fact is clearly manifested in the ^{1}H NMR spectra of the above-mentioned compounds (Table 17). The spectra of the unsymmetrical dimers **12c**,**d** are of most interest. The signals for the protons of the NH groups in these spectra are observed as singlets at δ −2 and −3, which is indicative of the nonequivalence of the π-electron systems of the porphyrin fragments of these dimers. Neither the spectra of the unsubstituted dimers **12e**,**f** nor the spectra of the symmetrical compounds **12a**,**b** show analogous splitting of the signals for the protons of the NH groups. The spectra of the dimers **12a**,**b** have one singlet each at δ −2.27 and −1.90, respectively. The high-field signal (at δ −3.0) was assigned to the *meso*-unsubstituted porphyrin fragment in the dimers **12c**,**d**, while the low-field signal (at δ −2.1 or −1.95) was assigned to the *meso*-substituted porphyrin fragment.[81] The chemical shifts of the protons in these compounds correspond to those in the linear *meso*-bound dimers of porphyrins whose spectra have signals for the protons of the aliphatic alkyl groups at δ 1.0–4.0, signals for the *meso*-H atoms at δ 9.8–11.0 and signals for the protons of the NH groups at δ −2.0 and −3.0. The signals for the protons of the phenyl fragments are observed at δ 7.95–8.95. These chemical shifts have different values in the spectra of the dimers **12a**,**c** and **12b**,**d** (see Table 17). The multiplicities and intensities of the signals correspond to the assumed structures of the compounds.

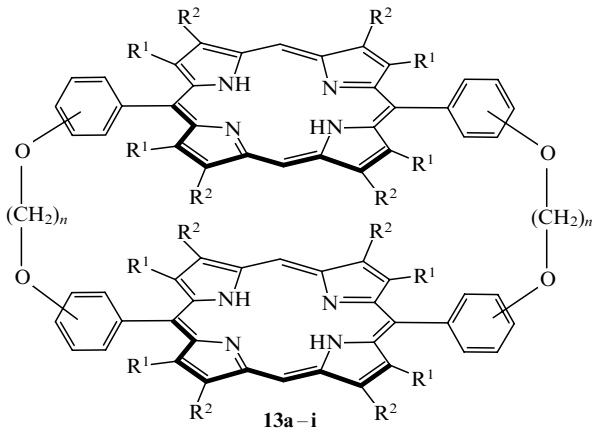


12a–**f**

$R^1 = R^2 =$ : Ar =  (**a**);  (**b**); R^1 = H, R^2 = :

Ar =  (**c**),  (**d**); $R^1 = R^2$ = H: Ar =  (**e**);  (**f**).

Dimeric *meso*-diphenyl-β-octaalkylporphyrins **13a**–**i** containing the bridging $O(CH_2)_nO$ groups at different positions of the phenyl substituent were investigated.[82–86]



13a–**i**

R^1 = Me, R^2 = Bu: n = 2, *para* (**a**); n = 3, *para* (**b**); n = 4, *para* (**c**); R^1 = Me, R^2 = Et: n = 3, *meta* (**d**); n = 4, *meta* (**e**); R^1 = Et, R^2 = Me: n = 4, *meta* (**f**); R^1 = Me, R^2 = Bu: n = 2, *ortho* (**g**); n = 3, *ortho* (**h**); n = 4, *ortho* (**i**).

The cyclophane structures of these compounds were confirmed by the ^{1}H NMR spectral data (Table 18). The *meso*-protons and the protons of the β-CH_3 and NH groups give singlet signals. This indicates that the dimers adopt a symmetrical conformation in which the porphyrin macrocycles are located one above the other. However, it is conceivable that the singlet signals are observed due to the time-averaging of different (including unsymmetrical) conformations of the porphyrins.

In the spectra of the dimers under consideration, the signals for the protons of the NH groups are shifted upfield compared to those of the monomeric analogues **3i**–**k**, which is a manifestation of the mutual magnetic shielding of the ring currents of the aromatic macrocycles. Judging from the positions of the signals, the distance between the porphyrin fragments increases as the length of the bridging group increases (see Table 18). This distance is responsible also for the upfield shifts of the signals for the protons of the methylene groups in the spectra of the compounds **13a**,**b**,**d**,**g**,**h** (in which the number of the methylene units in the bridges n = 2 and 3) compared to the signals for the protons of the methoxy groups in the spectra of *meso*-di(methoxyphenyl)-substituted monomeric porphyrins. Starting from n = 4, these signals in the spectra of both the dimeric and monomeric compounds are observed virtually in the same region regardless of the positions of the bridging units in the benzene rings of the compounds **13c**,**e**,**i**.

The chemical shifts of the β-alkyl protons change only slightly on going from the monomers to the corresponding dimers. However, these shifts are substantially different for different structural isomers. Thus, the dimers **13e**,**f** differ by the arrangement of the methyl and ethyl groups at the β positions of the porphyrin fragments. In the porphyrin **13e**, the protons of the methyl groups experience the shielding effect of the ring currents of the phenyl substituents. In the case of the dimer **13f**, the shielding effect is exerted on the protons of the ethyl groups. The maximum shifts (1.08 ppm) are observed for the protons of the methylene groups directly bound to the macrocycle, while virtually no shifts (0.02 ppm) are observed for the signals for the protons of the CH_3 groups.

The signals for the protons of the bridging OCH_2 groups and the signals for the protons of the OCH_3 groups of the monomeric analogues are located nearly in the same region. The protons of the bridging CH_2 groups give signals at $\delta \sim 1.90$, which is characteristic of the protons of the corresponding substituents in the monomeric porphyrins.[12] Apparently, this is attributable to the fact that the peripheral substituents are not virtually enclosed by the ring current of the conformationally flexible dimers.

The signals for the protons of the phenyl groups in the spectra of the dimers **13a**–**c** are observed as a doublet for the *ortho*-

Table 18. Positions and multiplicities of the signals in the ^{1}H NMR spectra of the dimeric porphyrins **13a**–**i** and their monomeric analogues **3i**–**k**.[82–86]

Compound	δ(NH)	δ(Alk)	δ(β-CH_3)	δ(H_{phenyl})			δ(H_{bridge})		δ(*meso*-H)
				2-H, 6-H	4-H	3-H, 5-H	CH_2	OCH_2	
13a	−5.27 s (4H)	1.03 t (24H), 1.63 m (16H), 2.10 m (16H), 3.90 t (16H)	2.39 s (24H)	7.80 d (8H)	–	7.10 d (8H)	–	4.01 t (8H)	9.10 s (4H)
13b	−4.92 s (4H)	0.98 t (24H), 1.36 m (16H), 2.11 m (16H), 3.84 t (16H)	2.41 s (24H)	7.84 d (8H)	–	7.14 d (8H)	2.01 m (4H)	3.92 t (8H)	9.43 s (4H)
13c	−4.64 s (4H)	1.00 t (24H), 1.48 m (16H), 2.12 m (16H), 3.87 t (16H)	2.42 s (24H)	7.81 d (8H)	–	7.24 d (8H)	1.94 m (8H)	3.90 t (8H)	10.12 s (4H)
3i	−2.38 s (2H)	1.03 t (12H), 1.67 m (8H), 2.10 m (8H), 3.85 t (8H)	2.42 s (12H)	7.82 d (4H)	–	7.13 d (4H)	–	3.98 s (6H) [a]	10.12 s (2H)
13d	−5.82 s (4H)	0.97 t (24H), 2.97 q (16H)	3.42 s (24H)	7.69 m (8H)	7.22 m (4H)	7.22 m (4H)	1.92 m (4H)	4.25 t (8H)	9.12 s (4H)
13e	−4.32 s (4H)	1.03 t (24H), 3.91 q (16H)	2.40 s (24H)	7.71 m (8H)	7.38 m (4H)	7.38 m (4H)	1.90 m (8H)	4.02 t (8H)	10.08 s (4H)
13f	−4.28 s (4H)	1.00 t (24H), 2.99 q (16H)	3.38 s (24H)	7.80 m (8H)	7.42 m (4H)	7.42 m (4H)	1.88 m (8H)	4.02 t (8H)	10.08 s (4H)
3j	−2.49 s (2H)	1.03 t (12H), 1.67 m (8H), 2.14 m (8H), 3.93 t (8H)	2.50 s (12H)	7.61 m (4H)	7.55 m (2H)	7.55 m (2H)	–	3.88 s (6H) [a]	10.18 s (2H)
13g [b]	–	0.98 t (24H), 1.36 m (16H), 2.01 m (16H), 3.85 t (16H)	2.50 s (24H)	7.74 m (4H)	7.36 m (4H)	7.36 m (8H)	–	4.06 t (8H)	9.08 s (4H)
13h [b,c]	–	0.96 t (24H), 1.48 m (16H), 2.12 m (16H), 3.84 t (16H)	2.46 s (24H)	7.70 d (4H)	7.21 t (4H)	7.64 t (4H) 7.12 d (4H)	1.98 m (4H)	4.01 t (8H)	9.52 s (4H)
13h [b,d]	–	0.99 t (24H), 1.52 m (16H), 2.12 m (16H), 3.87 t (16H)	2.48 s (24H)	7.60 m (4H)	7.19 t (4H)	7.65 m (4H) 7.11 d (4H)	2.01 m (4H)	4.03 t (8H)	9.50 s (4H)
13h [b,e]	–	1.01 t (24H), 1.49 m (16H), 2.13 m (16H), 3.86 t (16H)	2.49 s (24H)	7.57 m (4H)	7.17 t (4H)	7.65 m (4H) 7.11 d (4H)	2.04 m (4H)	4.11 t (8H)	9.54 s (4H)
13i [b]	–	1.07 t (24H), 1.57 m (16H), 2.07 m (16H), 3.89 t (16H)	2.44 s (24H)	7.82 m (4H)	7.42 m (4H)	7.42 m (8H)	1.96 m (8H)	3.94 s (8H)	10.09 s (4H)
3k	−2.38 s (2H)	1.09 t (12H), 1.67 m (8H), 2.18 m (8H), 3.99 t (8H)	2.53 s (12H)	7.67 d (2H)	7.19 t (2H)	7.60 t (2H) 7.10 d (2H)	–	3.66 s (6H) [a]	10.19 s (2H)

[a] Signals for the protons of the methoxy group; [b] zinc complexes. Atropoisomers of the zinc complex of the dimer **13h**: [c] α,α,α,α; [d] α,β,α,α; [e] α,β,α,β.

protons (at $\delta \sim 7.8$) and a doublet for the *meta*-protons (at $\delta \sim 7.15$).

The dimers linked through the *meta* (**13d**–**f**) or *ortho* positions (**13h**,**i**) of the phenyl substituents exist as three atropoisomers, which differ by the orientations of the oxygen atoms of the ether bridges (Fig. 4). The compound **13g** containing short ether bridges ($n = 2$) does not form atropoisomers. The assignment of the signals to particular atropoisomers was made based on comparison of the chromatographic mobilities and polarities of the porphyrin molecules. From Table 19 it can be seen that the experimental data (R_f) agree with the calculated characteristics (the dipole moments of the molecules). The smaller the dipole moment of the molecule, the higher the chromatographic mobility of the atropoisomer.

The atropoisomerism of porphyrins is well studied.[89,90] For the phenyl fragments to be rotated, the macrocycle must be deformed to reduce steric interactions between the *ortho*-substituents and the protons of the NH or CH_2 groups. The addition of the side methyl groups would be expected to hinder rotation. However, the activation energy of thermal atropoisomerism is increased only slightly on going from *meso*-tetraphenylporphyrin to (*meso*-diphenyl)octamethylporphyrin. This phenomenon was

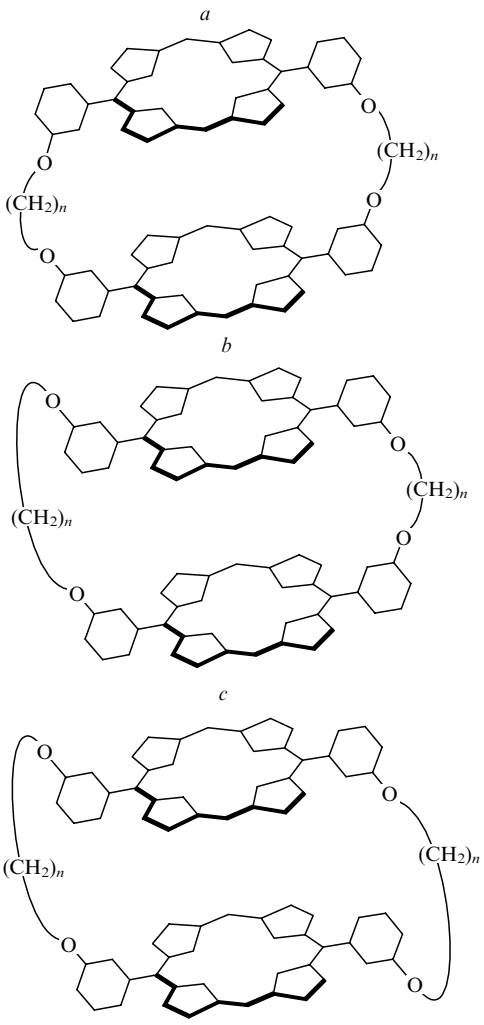


Figure 4. The α,α,α,α- (*a*), α,β,α,α- (*b*) and α,β,α,β-atropoisomers (*c*) of the dimers **12d**–**f**.[86]

accounted for by the flexibility of diphenylporphyrins.[89,90] The molecules of these compounds possess two free *meso* positions along which the ring is, apparently, folded. Therefore, steric restrictions arising from the introduction of additional β-methyl groups are compensated by flexibility of the diphenylporphyrin molecule.

It was demonstrated [12] that, unlike the monomeric porphyrin **3k**, which readily underwent atropoisomerisation in boiling *o*-xylene (starting from one isomer, a mixture of the α,α and α,β isomers was formed in a ratio of 1 : 1), the phenyl fragments in the dimeric porphyrins cannot rotate and the atropoisomers of these compounds are stable. The ^{1}H NMR spectral data for the α,α,α,α, α,β,α,α and α,β,α,β isomers of the zinc complex of the dimer **13h** are given in Table 18. As in the case of the monomer **3k**, the spectra of the atropoisomers of the dimeric porphyrin **13h** differ only by splitting of the signals for the protons of the phenyl groups. The spectrum of the α,α,α,α atropoisomer, which is, apparently, characterised by the higher degree of equivalence of the protons, has a doublet for the *ortho*-protons and a triplet for the *para*-protons. The nonequivalent *meta*-protons give individual signals as a doublet and a triplet. The spectra of the α,β,α,α and α,β,α,β atropoisomers have a pronounced triplet for the *para*-protons and a doublet from a portion of the *meta*-protons. The signals for the other portion of the *meta*-protons and the signals for the *ortho*-protons coalesce into a multiplet.

Table 19. Dipole moments (μ) and chromatographic mobilities (R_f) on Silufol of the monomeric (**3h**–**m**) and dimeric (**13h**) porphyrins.[87,88]

Compound	Substituent in the benzene ring	Atropoisomer	μ /D (see [a])	R_f (see [b])
3h	H		0.107	0.60
3i	4-OMe		0.681	0.43
3j	3-OMe		0.674	0.45
3k	2-OMe	α,α	0.970	0.30
		α,β	0.100	0.65
3l	4-NO_2		0.424	0.50
3m	3-NO_2		0.026	0.75
13h	2-O$(CH_2)_4$O-2	α,α,α,α	0.075	0.61
		α,β,α,α	0.755	0.49
		α,β,α,β	1.398	0.31

[a] The dipole moments were calculated by the semiempirical CNDO and INDO methods. The conformations with the minimum energies were optimised by the block-diagonal Newton–Raphson method; [b] in the case of monomeric porphyrins, the spots were visualised with toluene; in the case of the atropoisomers of the dimeric porphyrin, the spots were visualised with a 1 : 4 pyridine–hexane mixture.

IV. Electronic absorption spectra of porphyrins and metalloporphyrins

Electronic absorption spectra of porphyrins are very characteristic and contain four low-intensity absorption bands in the visible region and one very intense band in the violet region of the spectrum (the Soret band). The commonly accepted classification of these bands is as follows. The bands *I* and *III* in the visible region of the spectrum (Fig. 5 *a*) belong to quasi-forbidden electron transitions, whereas the bands *II* and *IV* are of electronic-vibrational origin, *i.e.*, are vibrational satellites of the bands *I* and *III*, respectively. Although possessing a number of common features, the spectra of porphyrins show substantial variations, which reflect the changes in the molecular structure and the effect of the solvent. According to the universally accepted concepts, light absorption is accompanied by excitation of the porphyrin molecule and the characteristic features of the absorption spectrum are determined by transitions of the π-electrons between two higher occupied and two lower unoccupied orbitals (the four-orbital Platt–Gouterman model [1]).

The intensity ratio of the absorption bands in the spectra of porphyrins depends on their structures in a peculiar fashion. The ethio type of the spectrum (see Fig. 5 *a*) with the intensity ratio *IV* > *III* > *II* > *I* is typical of *meso*-tetraphenylporphyrin, ethio-

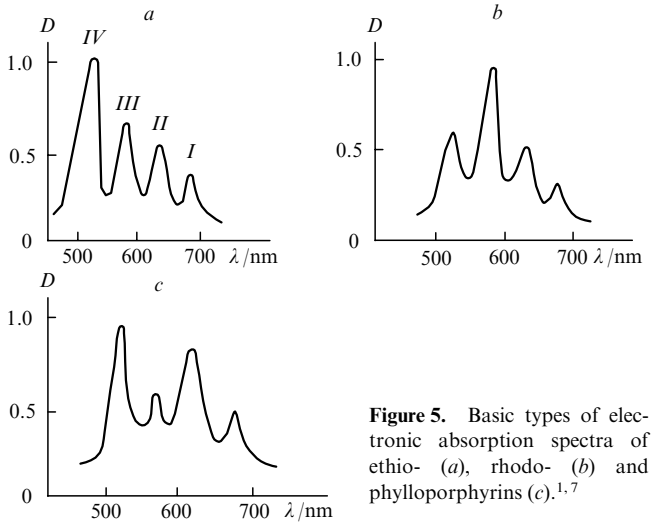


Figure 5. Basic types of electronic absorption spectra of ethio- (*a*), rhodo- (*b*) and phylloporphyrins (*c*).[1,7]

porphyrin and other symmetrically substituted porphyrins. For porphyrins characterised by the rhodo type of the spectra (Fig. 5 *b*), another sequence, *viz*., *III* > *IV* > *II* > *I*, is realised. Among the latter compounds are rhodoporphyrin and other porphyrins containing an electron-withdrawing substituent (COOH, NO_2, Cl, *etc*.) in the pyrrole fragment. Phylloporphyrin and other porphyrins containing one or two *meso*-substituents are characterised by the phyllo type of the spectrum (*IV* > *II* > *III* > *I*) (Fig. 5 *c*). Chlorin, tetrabenzoporphyrin and phthalocyanine give characteristic spectra of their own. In their spectra, the long-wavelength band *I* has the maximum intensity.

On going from porphyrin to metalloporphyrin, the symmetry of the planar macrocyclic fragment (of the π-electron cloud of the macrocycle) increases due to which the spectrum is simplified. The Soret band changes only slightly upon complex formation. The visible region of the spectra of metal complexes has two absorption bands, *viz*., the band *I* corresponding to the electron transition and the band *II* corresponding to the electronic-vibrational transition. The energy of the electron transition for the band *I* and its position in the spectrum (λ_1) can serve as reliable criteria for determining the strength and the type of the metal (M)—nitrogen chemical bond in metalloporphyrins. The band *I* is shifted hypsochromically as the strength of the M—N coordination bond in metalloporphyrins containing the planar MN_4 coordination unit increases.[91,92]

One of the most important features of metalloporphyrins is the deviation of the metal atom from the plane of the MN_4 coordination unit under the influence of the strongly coordinated molecular ligands or acido ligands. In most cases, the deviation of the metal atom from the plane is accompanied by a long-wavelength shift of the band *I*, whereas the movement of the metal atom toward the plane is accompanied by a short-wavelength shift.[7]

Therefore, electronic absorption spectroscopy is a powerful tool in studying the type and strength of the coordination bonds in metalloporphyrins, the degree of aromaticity of the macrocycle and its change upon chemical modification of the porphyrin.

1. Porphyrins

Electronic absorption spectra of porphyrins depend substantially on both the electronic and steric factors. Not only the positions and intensities of the absorption bands, but also their number can be changed. From this viewpoint, of special note is the introduction of four substituents at the *meso* positions of porphyrin. A rise in the aromaticity and an increase in the rigidity of the macrocycle lead to the complete disappearance of vibrational satellites and to a sharp increase in the intensities of the electron transition bands (Fig. 6). The band *I* in the electronic spectrum of tetraazoporphyrin is shifted to the short-wavelength region.[6]

On the whole, the introduction of substituents at the *meso* positions of the porphyrin macrocycle has a more substantial

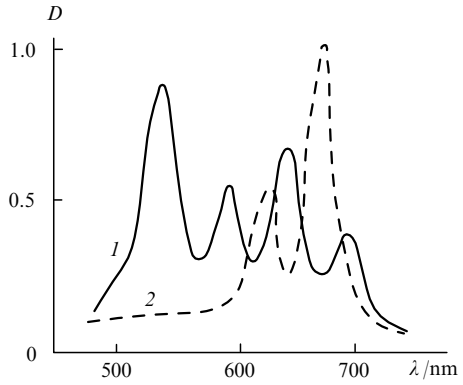


Figure 6. Electronic absorption spectra of porphyrin (*1*) and tetraazaporphyrin (*2*) in chloroform.[6,7]

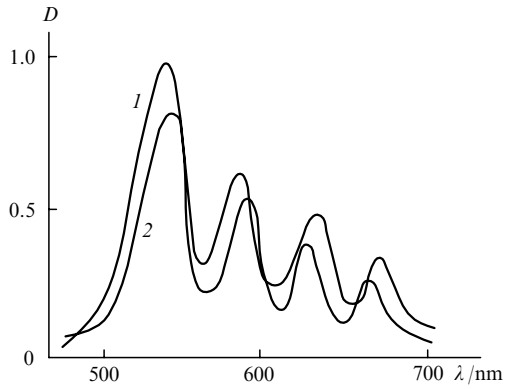


Figure 7. Electronic absorption spectra of *meso*-tetramethylporphyrin (*1*) and *meso*-tetraphenylporphyrin (*2*) in chloroform.[25]

effect on the absorption spectra than the introduction of substituents at the β positions. The *meso*-tetrasubstituted porphyrins are characterised by a distorted ethio type of spectra with rather large (25–40 nm) bathochromic shifts of the bands (Fig. 7, Table 20). It should be noted that small hypsochromic shifts of all absorption bands are observed on going from *meso*-tetramethylporphyrin to its homologues containing longer alkyl substituents.[38] Similar bathochromic shifts are observed in the electronic absorption bands on going from porphyrin to *meso*-tetraphenyl- or *meso*-tetramethylporphyrin (see Table 20). In these cases, the steric factor, apparently, prevails over the electronic effect.

The introduction of various substituents at the *para* positions of the phenyl rings of *meso*-tetraphenylporphyrin causes bathochromic shifts of the absorption bands in the visible region of the spectra. A comparison of the spectra of tetraphenylporphyrin and its *para*-substituted derivatives demonstrated that the intensities of the electron transition bands (*I* and *III*) rise as the electron-donating properties of the substituents increase. Simultaneously, the intensities of the vibrational bands (*II* and *IV*) are diminsihed.[93] The ethio type of the spectrum of tetraphenylporphyrin is distorted because the band *I* becomes more intense than the band *II*.

The presence of electron-donating substituents at the *meta* positions also leads to bathochromic shifts of the bands, the intensities of the vibrational bands being increased, while the intensities of the electron transition bands remaining virtually unchanged.[25] The spectra of *ortho*-substituted tetraphenylporphyrins are characterised by lower intensities of the electron transition bands compared to those observed in the electronic absorption spectrum of tetraphenylporphyrin. In some cases, this gives rise to the spectra of the phyllo type, for example, in the case of tetra(2-halogenophenyl)porphyrins and, particularly, in the case of tetra(2,6-dihalogenophenyl)porphyrins.

The absorption spectra are also dependent on the solvent. Thus, the bands in the electronic absorption spectra of substituted *meso*-tetraphenylporphyrins are shifted bathochromically and the intensities of the electron transition bands grow on going from nonpolar hexane to polar pyridine.[25]

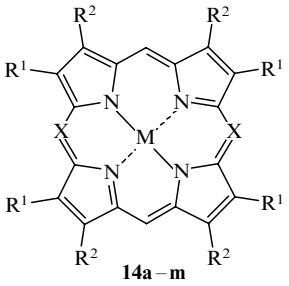
It is known[39] that the introduction of methyl groups at the β positions of the porphyrin ring causes only slight bathochromic shifts of the absorption bands (5–10 nm). The effect of the *meso*-substitution on the spectral characteristics of β-alkylporphyrins and their complexes with some transition metals (Zn, Cu or Ni) was investigated.[14,17,38,39] 2,8,12,18-Tetrabutyl-3,7,13,17-tetramethylporphyrin (**3t**), which is similar in the electronic effect of the substituents to natural porphyrins, was used as the starting compound. Derivatives of the porphyrin **3t** containing aryl (**3h**–**m**) or alkyl (**3a**–**g**) substituents or aza bridges (**14m**) at positions 5 and 15 are structurally related to the most important

Table 20. Electronic absorption spectra of *meso*-tetrasubstituted porphyrins in chloroform.[25,38]

meso-Substituents	λ_{max}/nm ($\varepsilon \times 10^{-3}$/litre mol^{-1} cm^{-1})				
	I	*II*	*III*	*IV*	Soret
H	615 (1.0)	562 (3.5)	515 (2.7)	490 (9.3)	394 (174)
H [a]	620 (4.4)	568 (6.3)	535 (9.1)	500 (12.1)	400 (141)
Me	664 (3.7)	610 (2.7)	560 (5.2)	524 (6.8)	420 (112)
Ph	648 (6.4)	590 (6.1)	550 (8.6)	516 (19.4)	419 (499)
Ph [b]	694 (9.1)	602 (8.0)	shoulder	553 (9.4)	454 (164)
4-$NH_2C_6H_4$	654 (7.6)	599 (5.5)	562 (12.0)	524 (12.0)	428 (313)
4-HOC_6H_4	650 (5.2)	595 (5.07)	556 (7.9)	519 (11.4)	423 (272)
4-$MeOC_6H_4$	652 (7.4)	595 (6.1)	557 (11.9)	520 (17.7)	423 (491)
4-$MeOC_6H_4$ (see [b])	703 (3.8)	608 (4.0)	shoulder	556 (5.27)	454 (189)
4-MeC_6H_4	648 (6.8)	593 (6.2)	554 (10.3)	518 (18.8)	412 (504)
4-BrC_6H_4	650 (6.5)	592 (7.4)	551 (10.6)	516 (21.9)	412 (567)
4-$NO_2C_6H_4$	650 (3.5)	592 (5.4)	552 (7.6)	518 (15.3)	426 (228)
4-$NO_2C_6H_4$ (see [b])	697 (3.8)	600 (3.9)	shoulder	552 (4.09)	454 (246)
3-$NH_2C_6H_4$	649 (3.9)	592 (5.2)	557 (7.1)	518 (15.1)	427 (155)
3-HOC_6H_4	645 (5.1)	588 (7.5)	550 (8.4)	514 (20.2)	419 (413)
3-$MeOC_6H_4$	648 (5.2)	590 (6.7)	550 (7.8)	516 (20.6)	420 (499)
3-MeC_6H_4	648 (6.5)	592 (6.0)	551 (8.7)	517 (18.7)	420 (485)
3-BrC_6H_4	652 (6.7)	592 (6.6)	549 (8.5)	516 (20.2)	420 (456)
3-$NO_2C_6H_4$	655 (6.6)	592 (7.1)	550 (7.3)	516 (20.6)	424 (352)
2-$NH_2C_6H_4$	653 (3.1)	595 (5.2)	556 (5.8)	519 (16.2)	422 (186)
2-HOC_6H_4	652 (5.6)	590 (5.3)	548 (5.6)	515 (16.6)	419 (354)
2-$MeOC_6H_4$	646 (4.1)	590 (7.6)	547 (7.3)	514 (21.9)	419 (432)
2-MeC_6H_4	648 (4.6)	590 (6.4)	546 (6.3)	515 (20.5)	418 (477)
2-BrC_6H_4	647 (2.6)	590 (7.7)	551 (4.3)	515 (22.5)	420 (475)
2-$NO_2C_6H_4$	654 (3.0)	596 (6.7)	552 (6.8)	518 (19.4)	424 (283)
C_6F_5	657 (4.4)	583 (8.0)	538 (4.1)	507 (22.3)	414 (317)

The spectral characteristics are given: [a] for β-octamethylporphyrin; [b] for *meso*-tetraaryl-β-octamethylporphyrins.

synthetic porphyrins, *viz*., to *meso*-tetraphenylporphyrin and tetraazaporphyrin.



14a–m

$R^1 = R^2 = Me$, X = CMe: M = Zn (**a**), Cu (**b**), Ni (**c**); R^1 = Me, $R^2 = Bu^n$: X = CPh, M = Zn (**d**), Cu (**e**), Ni (**f**); X = CH, M = Zn (**g**), Cu (**h**), Ni (**i**); X = N, M = Zn (**j**), Cu (**k**), Ni (**l**), H_2 (**m**).

As can be seen from Fig. 8, the absorption spectra of these compounds, as well as of their zinc complexes, are similar. The spectral changes are quantitative rather than qualitative. This fact indicates that the corresponding electron transitions are of the same type and suggests that the introduction of two phenyl or alkyl substituents or the replacement of the carbon atoms at the *meso* positions by the nitrogen atoms exerts a rather small perturbing effect on the π-system of the porphyrins and their zinc complexes under study, and the π-system retains the approximate symmetry D_{2h} and D_{4h}, respectively.

It was demonstrated [17] that electron transitions in metalloporphyrins occur from the a_{1u} and a_{2u} orbitals to the e_{gx} and e_{gy} orbitals. The a_{1u} orbital has four nodal planes passing through the *meso* positions and the central nitrogen atoms. The a_{2u} orbital possesses zero electron density on the β-carbon atoms. Hence, perturbation of the π-system of metalloporphyrins at the β positions, for example, upon alkylation, destabilises the a_{1u} orbital, while the energy level of the a_{2u} orbital remains unchanged. On the contrary, perturbation at the *meso* positions and the nitrogen atoms has no effect on the a_{1u} orbital and affects the a_{2u} orbital. Two degenerate antibonding e_g orbitals differ in that one of the nodal planes of the e_{gx} orbital and one of the nodal planes of the e_{gy} orbital pass through different pairs of the nitrogen atoms (in porphyrins, NH – NH).

Figure 9 shows the changes in the energy levels of the a_{1u}, a_{2u} and e_g orbitals (taking into account their nodal properties) that occur on going from the zinc complexes of the octaalkylporphyrin **14g** to the zinc complex of the *meso*-diazaoctaalkylporphyrin **14j**. The energy levels of the higher occupied (b_1 and b_2) and lower

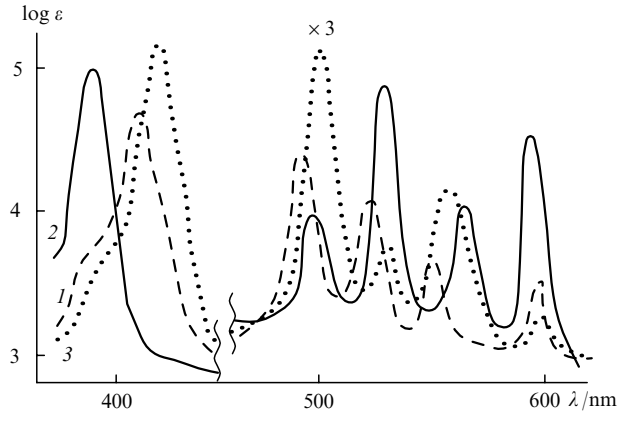


Figure 8. Electronic absorption spectra of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (*1*) and its 5,15-diaza- (*2*) and -diphenyl derivatives (*3*) in chloroform.[17]

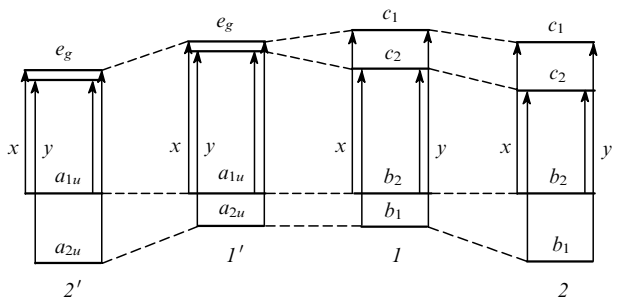


Figure 9. Scheme of the energy levels of the higher occupied and lower unoccupied orbitals of octaalkylporphyrin (*1*), its 5,15-diaza derivative (*2*) and their zinc complexes (*1′* and *2′*, respectively).[17]

unoccupied (c_1 and c_2) orbitals of free porphyrins are also presented in Fig. 9.

The replacement of the carbon atoms at the *meso* positions by the nitrogen atoms results primarily in lowering of the energy levels of the a_{2u} and e_g orbitals compared to the levels of these orbitals in the compound **14g** and, as a consequence, in weakening of the configuration interactions between the excited one-electron states $a_{1u}e_{gx}$ and $a_{2u}e_{gx}$ and between $a_{1u}e_{gy}$ and $a_{2u}e_{gy}$. Correspondingly, the intensity of the absorption band *I* in the electronic absorption spectrum of the complex **14j** is higher than that present in the spectrum of the complex **14g**. An analogous effect is observed in the case of free porphyrins. Thus, the bands *I* and *II* in the spectrum of the *meso*-diazaoctaalkylporphyrin **14m** are more intense than those in the spectrum of the octaalkylporphyrin **3t**.

Weakening of the configuration interaction would be expected to cause hypsochromic shifts of the absorption bands in the visible region of the spectra of the aza derivatives **14j**,**m** and the bathochromic shift of the Soret band. However, experimental studies demonstrated that the replacement of the carbon atoms by the nitrogen atoms has the opposite effect. Apparently, the direction of the shift of the absorption bands on going from the porphyrins **3t** and **14g** to their aza analogues **14m** and **14j** is determined by a change in the energy of the corresponding one-electron transitions, *i.e.*, by stabilisation of the a_{2u} and e_g levels in the compound **14j** and the b_1 and c_2 levels in the ligand **14m**. On going from the above-mentioned porphyrins to their aza derivatives, the intensities of the electronic-vibrational bands *II* and *IV* of the porphyrin and the band *II* of the complex are sharply diminished (see Fig. 8, Table 21). These bands borrow the intensity from the adjacent allowed Soret band.[17] The smaller the difference between the energies of the interacting transitions, the higher the efficiency of this rearrangement of the intensities. The replacement of the carbon atoms by the nitrogen atoms is accompanied by a

Table 21. Electronic absorption spectra of β-octaalkylporphyrin derivatives.[38, 39]

Compound	λ_{max} /nm (log ε)				
	I	*II*	*III*	*IV*	Soret
In chloroform					
3a	625.0 (2.98)	574.1 (3.17)	538.2 (3.21)	505.4 (3.77)	405.1 (4.61)
14a	–	570.3 (3.66)	537.1 (3.78)	–	408.6 (4.63)
14b	–	568.3 (3.58	534.1 (3.74)	–	405.7 (4.56)
14c	–	556.0 (3.42)	526.4 (3.19)	–	398.4 (4.17)
3b	626.3 (2.98)	572.4 (3.19)	539.0 (3.22)	509.4 (3.80)	405.3 (4.58)
3c	625.1 (2.93)	573.7 (3.15)	538.5 (3.20)	509.1 (3.79)	408.7 (4.60)
3d	626.3 (2.97)	572.7 (3.14)	539.7 (3.19)	509.2 (3.77)	405.1 (4.59)
3e	626.1 (2.94)	572.7 (3.13)	539.1 (3.19)	509.7 (3.76)	405.3 (4.56)
3f	626.3 (2.96)	573.0 (3.15)	539.4 (3.18)	508.4 (3.74)	407.1 (4.56)
3g	626.7 (2.91)	576.2 (3.14)	540.1 (3.17)	507.9 (3.76)	409.0 (4.62)
3h	622.0 (3.42)	574.7 (3.92)	541.1 (3.71)	508.1 (4.16)	409.8 (5.19)
14d	–	575.1 (3.99)	541.4 (4.26)	–	412.3 (5.08)
14e	–	573.2 (3.89)	539.6 (4.31)	–	410.4 (5.08)
14f	–	570.1 (3.79)	536.1 (4.28)	–	408.6 (5.14)
3i	623.6 (3.60)	572.1 (3.99)	542.4 (3.80)	508.4 (4.12)	409.4 (5.10)
3j	621.9 (3.49)	574.2 (3.71)	542.4 (3.60)	508.0 (4.01)	410.1 (5.14)
3k	622.4 (3.60)	573.8 (3.87)	541.8 (3.74)	508.2 (4.09)	409.0 (5.02)
3l	624.6 (3.41)	576.0 (3.70)	544.0 (3.52)	506.9 (4.16)	409.0 (5.17)
3m	622.5 (3.51)	576.4 (3.90)	543.0 (3.71)	507.1 (4.13)	410.4 (5.09)
14h	–	569.2 (3.86)	534.1 (3.54)	–	399.7 (5.17)
14i	–	557.1 (3.91)	526.1 (3.60)	–	396.7 (5.14)
3u	629.1 (3.48)	574.5 (3.62)	540.4 (3.68)	507.1 (4.01)	421.4 (4.89)
3v	634.5 (3.28)	576.1 (3.58)	542.1 (3.72)	508.4 (4.03)	422.1 (4.92)
14m	622.1 (4.01)	580.4 (3.64)	544.4 (4.17)	506.0 (3.69)	375.1 (5.20)
14j	–	589.3 (4.24)	548.5 (3.52)	–	378.6 (5.24)
14k	–	587.6 (4.14)	544.1 (3.41)	–	376.2 (5.14)
14l	–	576.4 (4.08)	536.4 (3.38)	–	370.1 (5.07)
In acetic acid					
3a	–	564.1 (3.89)	–	–	419.0 (5.24)
14a	–	570.3 (3.64)	537.0 (3.70)	–	405.1 (4.60)
3h	621.9 (3.78)	574.7 (4.03)	–	–	434.8 (5.21)
14d	621.9 (3.90)	574.7 (4.15)	–	–	434.0 (5.20)
3t	–	592.2 (3.49)	548.2 (3.81)	–	407.8 (5.08)
14g	–	592.4 (3.55)	548.7 (3.88)	–	407.2 (5.18)
14m	626.1 (3.81)	–	–	–	393.5 (5.10)
14j	624.6 (3.93)	–	–	–	379.9 (5.08)

hypsochromic shift of the Soret band resulting in the low intensities of the electronic-vibrational bands in the spectra of the compounds **14m** and **14j**.

A comparison of the electronic absorption spectra of the metal complexes of octaalkylporphyrin derivatives (M = Zn, Cu or Ni) demonstrated that the bands are shifted to the low-frequency region. These shifts increase in the series Zn < Cu < Ni, *i.e.*, as the strength of the metal–nitrogen coordination bond increases. An enhancement of the electronegativity of the metal atom leads to lowering of the electron density on the occupied π-orbitals of the porphyrin molecule, which is accompanied by hypsochromic shifts of the bands (particularly, of the band *I*).

An analogous regularity is also observed for the positions of the 'metal-sensitive' bands in the IR spectra of porphyrins.[11] The deformation vibration bands of the alkyl groups (at 955 and 910 cm^{-1}) and the stretching and deformation vibration bands of the *meso*-protons (at 3110, 1220 and 835 cm^{-1}) are shifted to the high-frequency region as the degree of coordination of the metal atom increases.

On going from the octaalkylporphyrin **3t** to the *meso*-diphenyloctaalkylporphyrin **3h**, the Soret band is shifted bathochromically (see Table 21). It was demonstrated [38] that the introduction of strong donor or acceptor substituents into the phenyl rings of the diphenyl-substituents porphyrins **3i**–**m** has virtually no effect on the absorption spectra. Apparently, all absorption bands are shifted bathochromically due to distortion of the planar structure of the porphyrin macrocycles due to the presence of the phenyl substituents. This suggestion is evidenced by the ^{1}H NMR spectral data.[12, 14] It is known that steric restrictions are responsible for analogous changes in the electronic absorption spectra of *ortho*-derivatives of tetraphenylporphyrin [81] and cyclophane dimeric porphyrin. [76] A comparison of the electronic absorption spectra of the structural isomers **3h** and **3n** showed that the replacement of the methyl groups at positions 3, 7, 13 and 17 of the porphyrin macrocycle by the butyl groups leads to a substantial increase in the bathochromic shift of the absorption bands resulting from additional deformation of the porphyrin molecule due to the mutual effect of the adjacent butyl and phenyl fragments.

The electronic absorption spectra of the *meso*-dialkyl-substituted octaalkylporphyrins **3a**–**g** belong to the ethio type. For the first four members of the series, the odd-even alternation of the positions of the bands *I* and *III* is observed (see Table 21).

The porphyrin rings in the *meso*-tetrasubstituted octaalkylporphyrins **3u**,**v** have distorted 'corrugated' structures giving rise to substantial bathochromic shifts and broadening of the bands in their electronic absorption spectra compared to those observed in the spectra of tetraphenylporphyrin and *meso*-disubstituted octaalkylporphyrins (see Table 21).

2. Bisporphyrins

The electronic absorption spectra of cyclophane dimeric porphyrins have the following distinguishing features as compared to the monomeric analogues:[76–86, 94–102]

(1) a relatively large hypsochromic shift and substantial broadening of the Soret band;

(2) one diffuse absorption band at the long-wavelength side of the Soret band;

(3) a small bathochromic shift in the visible region.

The shifts of the bands in the absorption spectrum are determined by two factors, *viz*., by essential interactions between two identical porphyrin fragments whose nature depends on the symmetry of the dimer (the factor of exciton interactions) and by the effect of the solvent, which reflects the different degree of solvation of the ground and excited states (the factor of solvation).

In the short-wavelength region, the effect of the first factor leads to the hypsochromic shift of the Soret band in the electronic absorption spectra of symmetrical porphyrins, while the second factor causes broadening of this band. The manifestation of the low-energy excited states is possible in the case of displacement or inclination of the porphyrin macrocycles due to which the Soret band has a shoulder at 450 nm. Small bathochromic shifts of the bands in the visible region are attributable to weakening of the effect of exciton interactions in the long-wavelength region of the spectrum.

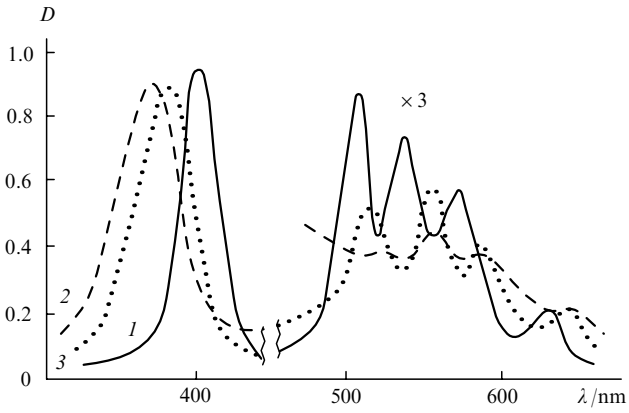


Figure 10. Electronic absorption spectra of the monomeric porphyrin **8** (*1*) and the dimeric porphyrins **7a** (*2*) and **7b** (*3*) in dichloromethane.[72]

The electronic absorption spectra of the monomeric porphyrin **8** and the β-bound dimers **7a**,**b**[72] are shown in Fig. 10.

The hypsochromic shift of the Soret band increases and the absorption bands in the visible region are shifted bathochromically and become more diffuse as the number of units in the bridge increases. The changes in the positions of the amide groups in the bridges also exert an effect on the electronic absorption spectra (Table 22).

In the electronic absorption spectra of the dimers **15a**–**d** and **16a**,**b** linked through the flexible hydrocarbon bridges and rigid aromatic fragments, respectively, the Soret band is shifted hypsochromically and the bands in the visible region are shifted bathochromically compared to those in the spectra of their monomeric analogues.[57, 70, 100] These shifts are determined by the strength of interactions between the porphyrin fragments, which depends not only on the distance between the macrocycles, but also on their mutual arrangement.

The hypsochromic shift of the Soret band in the electronic absorption spectrum of the compound **15c** containing two eight-atom bridges is 10 nm (Table 23). A decrease in the length of one bridge by two methylene units (the compound **15b**) leads to a

Table 22. Electronic absorption spectra of monomeric porphyrin (**8**) and the dimeric porphyrins **7a**–**n** in dichloromethane.[72, 73]

Compound	λ_{max} /nm				
	Soret	*IV*	*III*	*II*	*I*
7a	370	502	536	566	644
7b	376	502	544	577	626
7c	372	507	548	578	640
7d	381	–	–	–	627
7e	380	–	–	–	626
7f	384	–	–	–	624
7g	380	505	538	569	622
7h	382	–	–	554	–
7i	386	510	548	572	640
7j	392	–	526	566	–
7k	352	468	556	–	–
7l	382	473	534	560	–
7m	380	–	552	–	–
7n	384	–	520	558	–
8	400	498	536	566	620

Table 23. Electronic absorption spectra of monomeric and dimeric porphyrins in dichloromethane.[57, 70, 100]

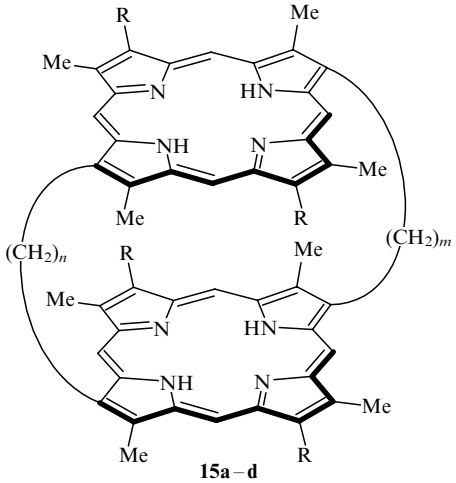
Compound	λ_{max}/nm				
	Soret	*IV*	*III*	*II*	*I*
2,7,12,17-Tetraethyl-3,8,13,18-tetramethylporphyrin	396	496	531	566	619
15a	385	498	532	567	620
15b	390	497	531	567	620
15c	386	501	534	569	623
15d	392	502	535	570	622
16a	394	503	537	572	625
16b	378	508	542	578	630
2,8,13,17-Tetraethyl-3,7,12,18-tetramethyl-5-phenylporphyrin	402	501	537	559	626

Table 24. Characteristics of absorption and emission of the porphyrins **8** and **17**.[94, 103]

Compound	λ/nm [a]	λ_{em}/nm [b]	ϕ_{rel} [c]
8	397	621	1.0
8 [d]	402	572	1.0
8 [e]	401	596	1.0
17a	385	624	0.54
17b	388	581	0.20
17c	397	596	0.71

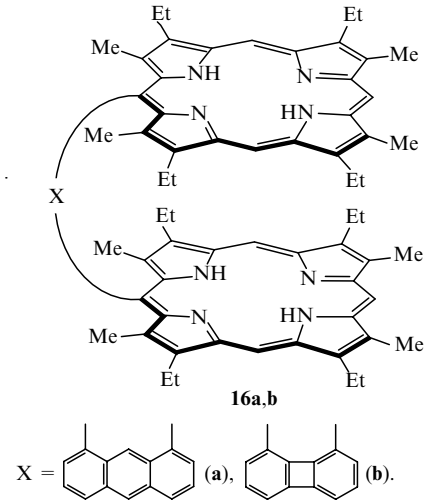
[a] The absorption maximum of the Soret band; the electronic absorption spectrum was measured in dichloromethane; [b] the emission spectrum was recorded in dichloromethane on irradiation in the Soret region; [c] the quantum yield of fluorescence of the dimeric complexes with respect to the corresponding monomeric complexes; [d] the Zn complex of the compound **8**; [e] the protonated form of the compound **8**.

decrease in this shift by 4 nm. Apparently, the interactions between the π-electron systems of the macrocycles are weakened and the effect of exciton interactions on the spectral properties is reduced due to inclination of the porphyrin macrocycles arising from the different length of the bridges. An analogous spectral behaviour was observed [94, 103, 104] in the case of dimers containing two flexible ester bridges.



15a–d

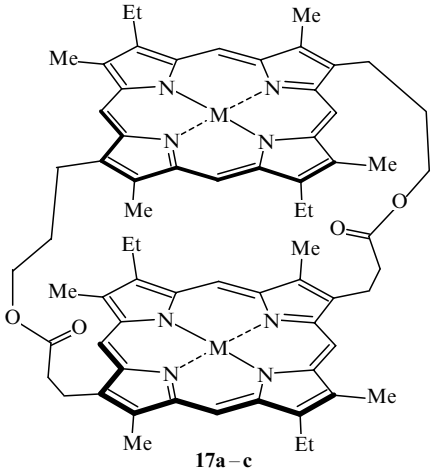
$m = n = 5$ (**a**), $m = 8$, $n = 6$ (**b**), $m = n = 8$ (**c**), $m = n = 10$ (**d**).



16a,b

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

The Soret band in the electronic absorption spectra of the dimer **17a** and its zinc complex **17b** is broadened and is hypsochromically shifted relative to the Soret band in the spectra of the monomer **8** and its zinc complex. The distance between the macrocycles in the dimers increases and interactions between the porphyrin fragments are weakened upon protonation (Table 24).



17a–c

M = H_2 (**a**), Zn (**b**), H_4 (**c**).

The dimers adopting a 'face-to-face' conformation are characterised by fluorescence quenching due to interactions between the porphyrin fragments. In the case of the dimer **17a**, this quenching was ~50% of the corresponding value for the monomeric analogue.

In the absorption spectra of the dimers containing four bridges, no hypsochromic shift is observed in the short-wavelength region (Table 25). The spectrum of the dimer **18a** containing the ester bridges is characterised (Fig. 11) by noticeable broadening and the bathochromic shift of the band in the visible region of the spectrum, while the position of the Soret band

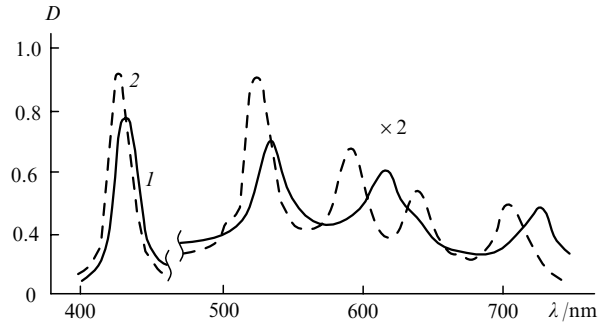


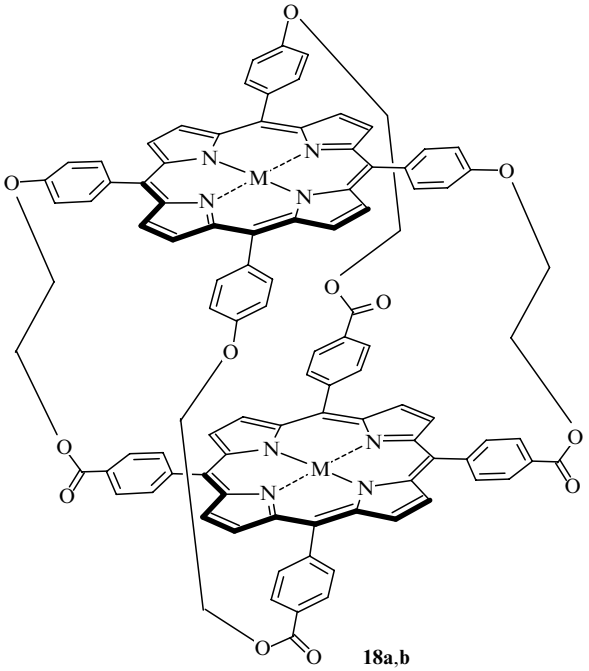
Figure 11. Electronic absorption spectra of the dimer **18a** (*1*) and tetra-*meso*-[*p*-2-(hydroxyethoxy)phenyl]porphyrin (*2*) in pyridine.[105]

Table 25. Electronic absorption spectra of monomeric and dimeric porphyrins in pyridine.[77, 104]

Compound	λ_{max} /nm				
	Soret	*IV*	*III*	*II*	*I*
11a	444	–	542	581	694
11b	446	–	–	620	666
11c	435	533	572	675	694
11e [a]	414	515	550	590	646
11f [a]	414	516	550	591	649
11g [a]	415	517	552	593	650
Tetra(*m*-butoxyphenyl)-porphyrin	420	515	550	594	651
Zn complex of tetra-(*m*-butoxyphenyl)-porphyrin	433	–	558	597	–
18a	426	523	562	584	677
18b	422	–	562	606	–

[a] The spectra were measured in chloroform.

remains unchanged.[70, 105] The absorption bands in the visible region of the spectrum of the dimer **11a** containing ether bonds are shifted bathochromically [77] by 25–40 nm and the Soret bands are shifted by 20–25 nm compared to those observed in the spectrum of the monomeric analogue (Fig. 12 *a*).



18a,**b**

M = H_2 (**a**), Zn (**b**).

This spectral behaviour of the dimer **11a** is attributed to extension of the conjugated π-electron system due to partial conjugation between the π-systems of the phenyl rings and the porphyrin macrocycles.[77] This effect is most clearly pronounced in the electronic absorption spectrum of a solution of the compound **11a** in CH_3CO_2H in which the dimer **11a** exists in the protonated form (Fig. 12 *b*).

Protonation leads to an essential increase of deformation of the macrocycle, while the dihedral angle between the mean porphyrin plane and the plane of the benzene π-systems decreases significantly. A decrease in the length of the bridge by one methylene group on going from the dimer **11a** to the dimer **11c** is accompanied by hypsochromic shifts of all bands by 7–21 nm (see Table 25). However, the bathochromic shift with respect to

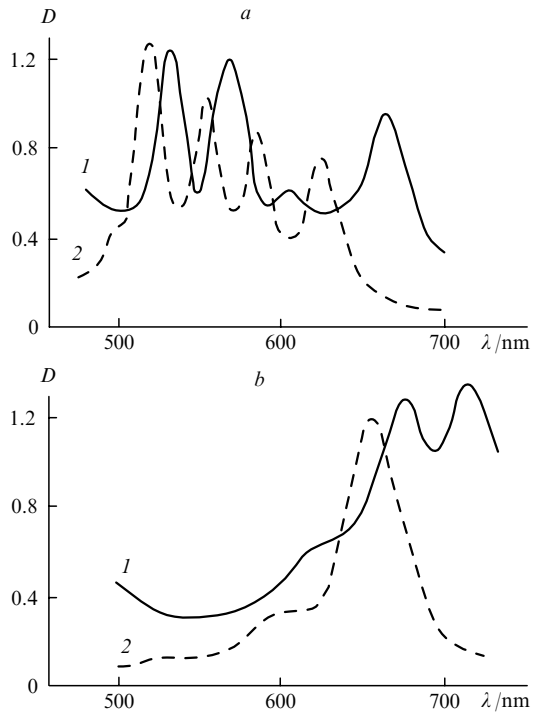


Figure 12. Electronic absorption spectra of the dimer **11a** (*1*) and tetra-*meso*-(*m*-butoxyphenyl)porphyrin (*2*) in pyridine (*a*) and acetic acid (*b*).[77]

the absorption bands in the spectrum of the monomeric analogue is retained.

In the electronic absorption spectra of the cyclophane dimers **11e**–**g**, the Soret band is shifted to the short-wavelength region by 4–5 nm and is broadened compared to the Soret band in the spectrum of the monomer (see Table 25).[79] Broadening is more pronounced in the case of the dimer **11f** in which the porphyrin fragments, while remaining parallel, are rotated with respect to each other (α_{max} = 26°). The spectral characteristics are changed due to interactions between the dipoles of the electronic transitions in two porphyrin fragments located at angles other than 0 or 180° with respect to each other. Bookser and Bruice [79] believed that the observed broadening and shifts of the bands indicate that solutions contain the dimers **11e**–**g** predominantly in a twist conformation. In this case, steric restrictions are less significant and the adjacent porphyrin rings are brought into proximity, which is also confirmed by the ^{1}H NMR spectral data.

The electronic absorption spectra (Fig. 13 *a*,*b*) of the dimeric *meso*-diphenyl-β-octaalkylporphyrins **13a**–**i** containing the $O(CH_2)_nO$ bridging groups were investigated.[82–85] The absorption bands of all dimeric porphyrins **13** are broadened and shifted hypsochromically by 5–20 nm compared to those in the spectrum of the monomeric porphyrin **3h** (Table 26). The short-wavelength shifts of the bands increase regularly as the length of the $O(CH_2)_nO$ bridge decreases and the adjacent porphyrin fragments approach each other. Considering this shift as a characteristic of the average distance between the porphyrin fragments in the dimer, it can be concluded that this distance decreases on going from the α,α,α,α to α,β,α,β atropoisomer (see Fig. 4). Calculations of the structures of the octamethyl analogues of the dimers by molecular mechanics demonstrated that the distance between the porphyrin fragments is no less than 3.6 Å.[87]

Consequently, exciton interactions between the porphyrin rings are responsible for the shifts of the absorption bands. Since the bands are shifted hypsochromically, the dimers have predominantly the 'face-to-face' orientation with the parallel arrangement of the interacting dipole moments of the electronic transitions. Each atropoisomer of the dimer exists as an equilibrium mixture of a large number of conformers. The structures of some of these

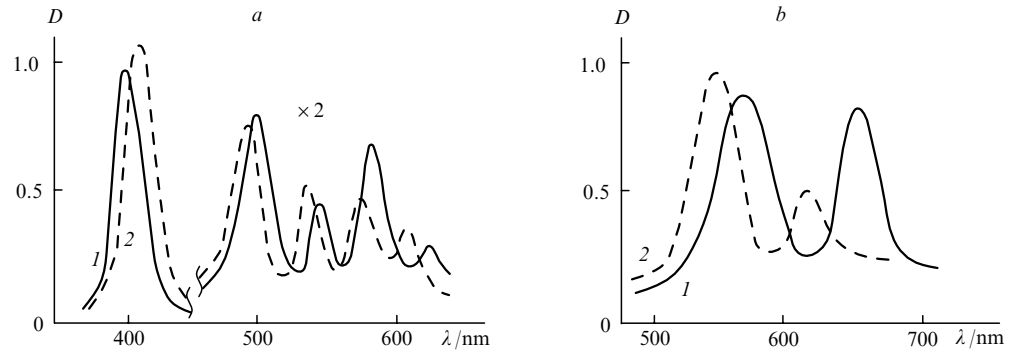


Figure 13. Electronic absorption spectra of the porphyrin **3h** (*1*) and the *meta*-bound dimer **13d** (*2*) in chloroform (*a*) and acetic acid (*b*).[82, 83]

Table 26. Electronic absorption spectra of the dimeric porphyrins **3h** and **13a**–**i**.[83, 86]

Compound	λ_{max}/nm (log ε)				
	Soret	*IV*	*III*	*II*	*I*
In chloroform					
3h	411 (5.35)	506 (4.21)	540 (3.81)	576 (3.89)	630 (3.45)
13a	405 (4.33)	503 (3.81)	538 (3.38)	573 (3.59)	626 (3.01)
13b	407 (4.91)	506 (3.99)	537 (2.45)	575 (3.63)	627 (3.19)
13c	410 (4.96)	507 (4.06)	540 (3.31)	576 (3.57)	629 (3.07)
13d [a]	393 (5.01)	497 (4.15)	531 (3.80)	565 (3.54)	621 (3.28)
13d [b]	395 (4.98)	497 (4.09)	534 (3.72)	568 (3.48)	622 (3.39)
13d [c]	394 (5.04)	496 (4.11)	530 (3.79)	566 (3.51)	621 (3.40)
13e [a]	395 (5.00)	498 (3.94)	534 (3.56)	569 (3.19)	623 (3.01)
13e [b]	396 (5.07)	500 (3.96)	537 (3.58)	571 (3.27)	623 (3.08)
13e [c]	395 (5.01)	497 (3.98)	533 (3.69)	569 (3.49)	622 (3.11)
13f [a]	397 (5.11)	501 (4.06)	541 (3.89)	573 (3.50)	624 (3.28)
13f [b]	399 (5.01)	503 (4.11)	542 (3.82)	576 (3.49)	625 (3.37)
13f [c]	397 (5.07)	500 (4.03)	539 (3.82)	576 (3.52)	623 (3.42)
13g	386 (5.10)	494 (3.96)	530 (3.60)	566 (3.27)	618 (3.08)
13h [a]	390 (4.99)	495 (3.92)	531 (3.56)	563 (3.26)	619 (3.08)
13h [b]	391 (4.92)	496 (3.89)	533 (3.42)	566 (3.36)	620 (3.13)
13h [c]	390 (4.99)	495 (3.92)	531 (3.56)	563 (3.26)	619 (3.08)
13i [a]	391 (5.08)	495 (3.90)	530 (3.57)	561 (3.28)	619 (3.07)
13i [b]	393 (5.00)	498 (3.87)	535 (3.52)	566 (3.21)	620 (3.04)
13i [c]	393 (5.01)	496 (3,94)	533 (3.60)	562 (3.20)	620 (3.00)
In acetic acid					
3h	436 (5.38)	–	572 (4.16)	–	619 (3.88)
13a	432 (4.90)	–	556 (4.51)	–	589 (3.17)
13b	435 (4.96)	–	558 (4.37)	–	593 (3.29)
13c	438 (4.93)	–	559 (4.09)	–	597 (3.11)
13d [a]	435 (4.92)	–	552 (4.42)	–	591 (3.59)
13d [b]	436 (4.87)	–	552 (4.40)	–	590 (3.50)
13d [c]	435 (4.96)	–	552 (4.42)	–	590 (3.54)
13e [a]	438 (4.91)	–	552 (4.42)	–	595 (3.51)
13e [b]	437 (4.90)	–	552 (4.48)	–	595 (3.49)
13e [c]	438 (4.94)	–	552 (4.45)	–	595 (3.54)
13f [a]	440 (4.92)	–	555 (4.43)	–	592 (3.35)
13f [b]	439 (4.81)	–	555 (4.43)	–	592 (3.29)
13f [c]	439 (4.86)	–	556 (4.45)	–	592 (3.54)
13g	427 (4.90)	–	549 (4.48)	–	583 (3.47)
13h [a]	430 (4.87)	–	550 (4.27)	–	587 (3.61)
13h [b]	431 (4.73)	–	551 (4.14)	–	588 (3.40)
13h [c]	430 (4.81)	–	550 (4.39)	–	587 (3.52)
13i [a]	433 (4.73)	–	551 (4.37)	–	591 (3.62)
13i [b]	434 (4.60)	–	552 (4.19)	–	591 (3.36)
13i [c]	434 (4.86)	–	552 (4.41)	–	592 (3.50)

Atropoisomers: [a] α,α,α,α; [b] α,β,α,α; [c] α,β,α,β.

conformers were studied by molecular mechanics (the MM+ force field). The atomic coordinates and the components of the potential energy of the optimised structures are summarised in the study.[87] From Table 27 it follows that a change from one conformer to another is generally accompanied by insignificant changes in the energy of the molecule (at most 10 kJ mol^{-1}). In spite of the fact that it is presently impossible to carry out complete analysis of the potential energy surface of such complex molecules, the existence of various conformational isomers in the gaseous phase and solutions is beyond question.

The results of geometry optimisation of dimeric porphyrins by the MM+ method (Fig. 14) demonstrated [87,88] that the aromatic tetrapyrrole macrocycle is deformed very readily. None of 15 conformers contains the planar porphyrin fragment. Conformational rearrangements of the tetrapyrrole nucleus occur through changes of the dihedral angles C–C–C–C, C–C–C–N, *etc.*, while the bond lengths and bond angles remain constant.

Each conformer of the dimeric porphyrins **13a**–**i** has its own individual absorption spectrum. It is needless to say that these spectra are qualitatively similar to the spectra of the monomeric analogues. However, in a quantitative sense these differences may be significant. One would expect that the absorption bands of the conformers with the parallel and perpendicular arrangement of the porphyrin rings will be shifted hypsochromically and bathochromically, respectively, under the influence of the exciton factor. The experimental spectra represent superpositions of the spectra of all conformers present in solution due to which the absorption bands of dimeric compounds are broadened and their intensities are lower compared to those of monomeric porphyrin. At the same time, the corresponding absorption bands in the spectra of monomeric and dimeric porphyrins do not differ in oscillator strength (f), which was calculated according to the approximate equation

$$f = (4.6 \times 10^{-9})\, \varepsilon_{max} \Delta\nu_{1/2},$$

where ε_{max} is the absorption coefficient at the absorption maximum and $\Delta\nu_{1/2}$ is the half-width of the band.

The data in Table 26 show that the absorption bands in the spectra of the *para*-bound dimers **13a**–**c** are shifted bathochromically compared to those of their *meta*- (**13d**–**f**) and *ortho*-analogues (**13g**–**i**). This phenomenon may be attributed both to an increase in the proportion of conformers of the 'half-open shell' type and to a more substantial deformation of the porphyrin macrocycle in the *para*-bound dimers.

Table 27. Strain energies of the conformers of the *ortho*-, *meta*- and *para*-bound dimers **13a**,**d**,**h** (E/kJ mol^{-1}) and their components (kJ mol^{-1}): strain energies of bonds (E_1), bond angles (E_2), torsion angles (E_3), van der Waals interactions (E_4), stretching–bending (E_5) and Coulomb interactions (E_6).[87,88]

Compound **13**	Conformer [a]	E	E_1	E_2	E_3	E_4	E_5	E_6
h	*1*	650	19	412	78	74	3	56
	2	653	20	421	86	71	1	56
	3	684	20	453	91	63	1	56
d	*4*	618	18	430	78	35	1	55
	5	599	18	423	83	20	1	54
	6	646	20	425	80	65	1	54
	7	623	20	424	85	40	1	52
	8	654	18	421	81	79	1	54
	9	591	18	419	81	14	1	58
a	*10*	669	21	431	72	90	2	53
	11	674	20	423	92	84	1	54
	12	683	21	437	99	71	2	53

[a] For notations of the conformers, see Fig. 14.

It should be noted that not only the positions of the absorption bands, but also the ratio of their intensities in the electronic absorption spectra of dimeric porphyrins are changed. In the case of *para*-bound dimers, the phyllo type of the spectrum, which is characteristic of monomeric β-octaalkyl-*meso*-diphenylporphyrins, is retained, while the spectra of the *ortho*- and *meta*-analogues belong to the ethio type (Fig. 15).

The differences in the electronic absorption spectra are reduced due to protonation of the porphyrin rings of the dimers **13a**–**i** in acetic acid and, correspondingly, to an increase of the distance between the likely charged fragments.

* * *

The data surveyed in the present review give convincing evidence that the combined use of modern spectroscopic methods enables one to obtain comprehensive information on the molecular

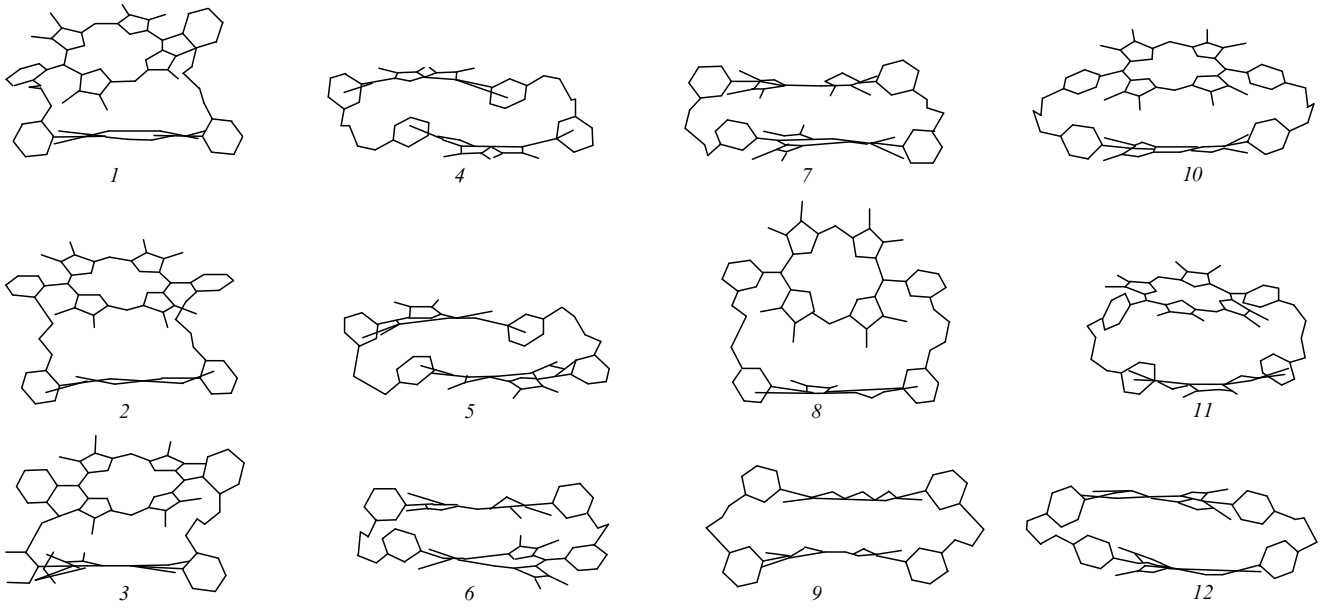


Figure 14. Conformers of the dimeric porphyrins **13h** (*1*–*3*), **13d** (*4*–*9*) and **13a** (*10*–*12*).[87,88]

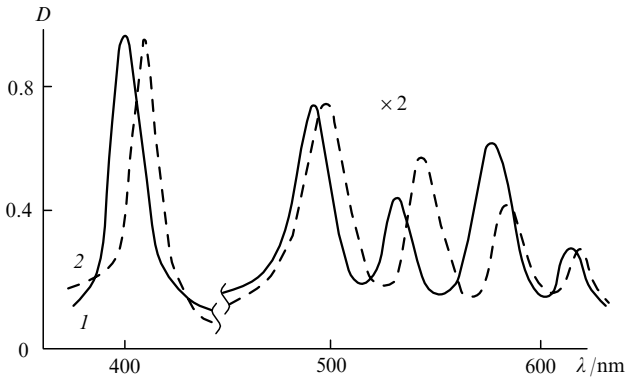


Figure 15. Electronic absorption spectra of the dimers **13a** (*1*) and **13d** (*2*) in chloroform.[83, 86]

structures of the newly synthesised compounds. The development of the spectroscopy of porphyrins provides the theoretical basis for the wider use of this unique class of tetrapyrrole macrocyclic compounds in technology, medicine and biology because the determination of the correlations between the structure and the spectral properties of the molecules can help in solving the problem of the construction of new materials with the desired properties.

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References

1. G P Gurinovich, A N Sevchenko, K N Solov'ev *Spektroskopiya Khlorofilla i Rodstvennykh Soedinenii* (Spectroscopy of Chlorophyll and Related Compounds) (Minsk: Nauka i Tekhnika, 1968)
2. K N Solov'ev, L L Gladkov, A S Starukhin *Spektroskopiya Porfirinov: Kolebatel'nye Sostoyaniya* (Spectroscopy of Porphyrins: Vibrational States) (Minsk: Nauka i Tekhnika, 1985)
3. M Gouterman *J. Chem. Phys.* **30** 1139 (1959)
4. M Gouterman *J. Mol. Spectrosc.* **6** 138 (1961)
5. A H Corwin, A B Chivvis, R W Poor, D G Whitten, E W Baker *J. Am. Chem. Soc.* **90** 6577 (1968)
6. B D Berezin *Koordinatsionnye Soedineniya Porfirinov i Ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine) (Moscow: Nauka, 1978)
7. B D Berezin, N S Enikolopyan *Metalloporfiriny* (Metalloporphyrins) (Moscow: Nauka, 1988)
8. V A Kuz'mitskii, K N Solov'ev, M P Tsvirko, in *Porfiriny: Spektroskopiya, Elektrokhimiya, Primenenie* (Porphyrins: Spectroscopy, Electrochemistry, Applications) (Ed. N S Enikolopyan) (Moscow: Nauka, 1987) p. 7
9. N Zh Mamardashvili, O A Golubchikov *Zh. Org. Khim.* **35** 1080 (1999) [a]
10. N Zh Mamardashvili, M E Klueva, O A Golubchikov *Molecules* **5** 89 (2000)
11. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Pirroly. Raschet Metodom Molekulyarnoi Mekhaniki* (Pyrroles. Molecular Mechanics Calculation); article deposited at the VINITI No. 3133-V97 (Moscow, 1996)
12. N Zh Mamardashvili, A S Semeikin, L V Klopova, O A Golubchikov, in *XIII Vsesoyuz. Seminar po Khimii Porfirinov i ikh Analogov (Tez. Dokl.), Samarkand, 1991* [The XIIIth All-Union Seminar on the Chemistry of Porphyrins and Their Analogues (Abstracts of Reports), Samarkand, 1991] p. 98
13. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Zh. Org. Khim.* **34** 1234 (1998) [a]
14. N Zh Mamardashvili, A S Semeikin, O A Golubchikov *Zh. Org. Khim.* **29** 1213 (1993) [a]
15. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Dipirrolilmetany. Raschet Metodom Molekulyarnoi Mekhaniki* (Dipyrrolylmethanes. Molecular Mechanics Calculation); article deposited at the VINITI No. 1470-V97 (Moscow, 1997)
16. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Geometricheskie Parametry Dipirrolilmetanov. Raschet Metodom Molekulyarnoi Mekhaniki* (Geometric Parameters of Dipyrrolylmethanes. Molecular Mechanics Calculation); article deposited at the VINITI No. 1697-V97 (Moscow, 1997)
17. A S Semeikin, N Zh Mamardashvili, A V Glazunov, O A Golubchikov, B D Berezin *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **33** (9) 12 (1990)
18. N Zh Mamardashvili, A S Semeikin, O A Golubchikov, B D Berezin, in *XVII Vsesoyuz. Chugaevskoe Soveshch. po Khimii Kompleksnykh Soedinenii (Tez. Dokl.), Minsk, 1990* [The XVIth All-Union Chugaev Meeting on the Chemistry of Complex Compounds (Abstracts of Reports), Minsk, 1990] p. 120
19. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov, in *Problemy Sol'vatatsii i Kompleksoobrazovaniya v Rastvorakh (Tez. Dokl. VI Mezhdunar. Konf.), Ivanovo, 1995* [The Problems of Solvation and Complex-Formation in Solutions (Abstracts of Reports of the VIth International Conference), Ivanovo, 1995] N23
20. N Zh Mamardashvili, A S Semeikin, O A Golubchikov, B D Berezin, in *III Vsesoyuz. Konf. po Khimii i Biokhimii Makrotsiklicheskikh Soedinenii (Tez. Dokl.), Ivanovo, 1988* [The Third All-Union Conference on the Chemistry and Biochemistry of Macrocyclic Compounds (Abstracts of Reports), Ivanovo, 1988] p. 318
21. N Zh Mamardashvili, O A Golubchikov *Molecules* **5** 757 (2000)
22. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Struktura 5,15-Difenilzameshchennykh β-Oktalkilporfirinov. Raschet Metodom Molekulyarnoi Mekhaniki* (The Structure of 5,15-Diphenyl-Substituted β-Octaalkylporphyrins. Molecular Mechanics Calculation); article deposited at the VINITI No. 3703-V97 (Moscow, 1997)
23. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Geometricheskie Parametry 5,15-Difenilzameshchennykh β-Oktalkilporfirinov. Raschet Metodom Molekulyarnoi Mekhaniki* (Geometrical Parameters of 5,15-Diphenyl-Substituted β-Octaalkylporphyrins. Molecular Mechanics Calculation); article deposited at the VINITI No. 3704-V97 (Moscow, 1997)
24. S A Zdanovich, N Zh Mamardashvili, O A Golubchikov *Zh. Org. Khim.* **32** 788 (1996) [a]
25. A S Semeikin, Doctoral Thesis in Chemical Sciences, Ivanovo Chemical Technological Institute, Ivanovo, 1995
26. S F Mason *J. Chem. Soc.* 976 (1958)
27. N Zh Mamardashvili, A M Semeikin, S A Zdanovich, O A Golubchikov, in *Pervaya Mezhdunar. Konf. po Biokoordinatsionnoi Khimii (Tez. Dokl.), Ivanovo, 1994* [The First International Conference on Biocoordination Chemistry (Abstracts of Reports), Ivanovo, 1994] p. 195
28. T A Koroleva, O I Koifman, B D Berezin *Zh. Fiz. Khim.* **55** 2007 (1981) [b]
29. R M Silverstein, G C Bussler, T C Morrill *Spectrometric Identification of Organic Compounds* (New York: Wiley, 1974)
30. S A Syrbu, A S Semeikin, B D Berezin, in *Pervaya Mezhdunar. Konf. po Biokoordinatsionnoi Khimii (Tez. Dokl.), Ivanovo, 1994* [The First International Conference on Biocoordination Chemistry (Abstracts of Reports), Ivanovo, 1994] p. 198
31. H Ogoshi, N Masai, Z-i Yoshida, J Takemoto, K Nakamoto *Bull. Chem. Soc. Jpn.* **44** 49 (1971)
32. N V Ivashin, S N Terekhov, I F Gurinovich, V V Sivchik *Zh. Prikl. Spektrosk.* **34** 124 (1981)
33. N V Ivashin, I F Gurinovich, G P Gurinovich *Zh. Prikl. Spektrosk.* **23** 1026 (1975)
34. O I Koifman, Doctoral Thesis in Chemical Sciences, Ivanovo Chemical Technological Institute, Ivanovo, 1983
35. T N Lomova, B D Berezin *Koord. Khim.* **27** 96 (2001) [c]
36. T N Lomova, N I Volkova, B D Berezin *Zh. Neorg. Khim.* **30** 626 (1985) [d]
37. B A Suleiman, G E Nikitina, A S Semeikin, N Zh Mamardashvili, O A Golubchikov, in *XX Nauch. Sessiya Rossiiskogo Seminara po Khimii Porfirinov i ikh Analogov (Tez. Dokl.), Ivanovo, 1999* [The XXth Scientific Session of Russian Seminar on the Chemistry of Porphyrins and Their Analogues (Abstracts of Reports), Ivanovo, 1999] p. 7

38. N Zh Mamardashvili, A S Semeikin, O A Golubchikov, B D Berezin, in *Problemy Sol'vatatsii i Kompleksoobrazovaniya v Nevodnykh Rastvorakh (Tez. Dokl. IV Vsesoyuz. Soveshch.), Ivanovo, 1989* [The Problems of Solvation and Complex-Formation in Non-aqueous Solutions (Abstracts of Reports of the IVIth All-Union Meeting), Ivanovo, 1989] p. 211
39. N Zh Mamardashvili, A S Semeikin, L V Klopova, O A Golubchikov *ESP β-Oktalkil-ms-difenilporfirinov v Nevodnykh Rastvoritelyakh* (EAS of β-Oktaalkyl-ms-Diphenylporphyrins in Nonaqueous Solvents); article deposited at the VINITI No. 3733-V89 (Moscow, 1989)
40. H L Anderson, J K M Sanders *J. Chem. Soc., Perkin Trans. 1* 2223 (1995)
41. H L Anderson, S Anderson, J K M Sanders *J. Chem. Soc., Perkin Trans. 1* 2231 (1995)
42. S Anderson, H L Anderson, J K M Sanders *J. Chem. Soc., Perkin Trans. 1* 2247 (1995)
43. H L Anderson, C J Walter, A Vidal-Ferran, R A Hay, P A Lowden, J K M Sanders *J. Chem. Soc., Perkin Trans. 1* 2275 (1995)
44. C C Mak, N Bampos, J K M Sanders *Angew. Chem., Int. Ed. Engl.* **37** 3020 (1998)
45. T E Clement, D J Nurco, K M Smith *Inorg. Chem.* **37** 1150 (1998)
46. R Paolesse, R K Pandey, T P Forsyth, L Jaquinod, K R Gerzevske, D J Nurco, M O Senge, S Licoccia, T Boschi, K M Smith *J. Am. Chem. Soc.* **118** 3869 (1996)
47. T Hirao, K Saito *Tetrahedron Lett.* **41** 1413 (2000)
48. H Nasri, M Debbabi *Polyhedron* **17** 3607 (1998)
49. G V Ponomarev, G V Kirillova, G B Maravin, T A Babushkina, V P Suboch *Khim. Geterotsikl. Soedin.* **6** 776 (1979) [e]
50. C-B Wang, S K Chang *Synthesis* **7** 548 (1979)
51. C K Chang *J. Am. Chem. Soc.* **99** 2819 (1977)
52. H Ogoshi, H Sugimoto, T Nishiguchi, T Watanabe, Y Matsuda, Z Yoshida *Chem. Lett.* 29 (1978)
53. H Ogoshi, H Sugimoto, Z-i Yoshida *Tetrahedron Lett.* **49** 4477 (1976)
54. M J Crossley, M M Harding, S Sternhell *J. Am. Chem. Soc.* **108** 3608 (1986)
55. G M Dubowchik, A D Hamilton *J. Chem. Soc., Chem. Commun.* 665 (1986)
56. K Maruyama, T Nagata, N Ono, A Osuka *Bull. Chem. Soc. Jpn.* **62** 3167 (1989)
57. I Abdalmuhdi, C K Chang *J. Org. Chem.* **50** 411 (1985)
58. J P Collman, J I Brauman, T J Collins, B L Iverson, G Lang, R B Pettman, J L Sessler, M A Walters *J. Am. Chem. Soc.* **105** 3038 (1983)
59. J P Collman, C E Barnes, P N Swepston, J A Ibers *J. Am. Chem. Soc.* **106** 3500 (1984)
60. B Morgan, D Dolphin *J. Org. Chem.* **52** 5364 (1987)
61. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *PMR Spektry Mono-, Di- i Tetrapirrol'nykh Soedinenii Lineinogo i Tsiklicheskogo Stroeniya* (^{1}H NMR Spectra of Mono-, Di- and Tetrapyrrole Compounds with Linear and Cyclic Structures); article deposited at the VINITI No. 1616-V95 (Moscow, 1995)
62. H Ogoshi, E-i Watanabe, N Koketsu, Z-i Yoshida *Bull. Chem. Soc. Jpn.* **49** 2529 (1976)
63. Yu B Ivanova, N Zh Mamardashvili, V B Sheinin, O A Golubchikov, in *Problemy Sol'vatatsii i Kompleksoobrazovaniya v Rastvorakh (Tez. Dokl. VII Mezhdunar. Konf.), Ivanovo, 1998* [The Problems of Solvation and Complex-Formation in Solutions (Abstracts of Reports of the VIIth International Conference), Ivanovo, 1998] p. 458
64. J Hiom, J B Paine III, U Zapf, D Dolphin *Can. J. Chem.* **61** 2220 (1983)
65. S Wolowiec *Polyhedron* **17** 1295 (1998)
66. T P Wijesekera, J B Paine III, D Dolphin *J. Am. Chem. Soc.* **105** 6747 (1983)
67. D A Ban, A F Mironov *Mendeleev Commun.* **4** 153 (1995)
68. E G Levinson, A F Mironov *Mendeleev Commun.* **3** 94 (1994)
69. A Osuka, K Maruyama, I Yamazaki, N Tamai *J. Chem. Soc., Chem. Commun.* 1243 (1988)
70. D Dolphin, J Hiom, J B Paine III *Heterocycles* **16** 417 (1981)
71. C K Chang, M-S Kuo, C-B Wang *J. Heterocycl. Chem.* **14** 943 (1977)
72. J P Collman, C S Bencosme, C E Barnes, B D Miller *J. Am. Chem. Soc.* **105** 2704 (1983)
73. J P Collman, F C Anson, C E Barnes, C S Bencosme, T Geiger, E R Evitt, R P Kreh, K Meier, R B Pettman *J. Am. Chem. Soc.* **105** 2694 (1983)
74. C K Chang *Adv. Chem. Ser.* **173** 162 (1979)
75. A Osuka, F Kobayashi, T Nagata, K Maruyama *Chem. Lett.* 287 (1990)
76. J A Anton, J Kwong, P A Loach *J. Heterocycl. Chem.* **13** 717 (1976)
77. O A Golubchikov, S G Korovina, E M Kuvshinova, A S Semeikin, A M Shul'ga, V A Perfil'ev, S A Syrbu, B D Berezin *Zh. Org. Khim.* **24** 2378 (1988) [a]
78. O A Golubchikov, in *Pervaya Mezhdunar. Konf. po Biokoordinatsionnoi Khimii (Tez. Dokl.), Ivanovo, 1994* [The First International Conference on Biocoordination Chemistry (Abstracts of Reports), Ivanovo, 1994] p. 188
79. B C Bookser, T C Bruice *J. Am. Chem. Soc.* **113** 4208 (1991)
80. G M Dubowchik, A D Hamilton *J. Chem. Soc., Chem. Commun.* 904 (1985)
81. J L Sessler, M R Johnson *Angew. Chem.* **99** 679 (1987)
82. N Zh Mamardashvili, A S Semeikin, B D Beresin, O A Golubchikov, in *Proceedings of the 3rd European Symposium on Organic Reactivity, Göteborg, 1991* p. 211
83. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Zh. Org. Khim.* **32** 934 (1996) [a]
84. N Zh Mamardashvili, A S Semeikin, S A Zdanovich, O A Golubchikov, in *Proceedings of the Vth European Symposium on Organic Reactivity, Santiago de Compostela, 1995* p. 170
85. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov, in *VII Mezhdunar. Konf. po Khimii Porfirinov i ikh Analogov (Tez. Dokl.), S.-Peterburg, 1995* [The VIIth International Conference on the Chemistry of Porphyrins and Their Analogs (Abstracts of Reports), St. Petersburg, 1995] p. 22
86. O A Golubchikov, N Zh Mamardashvili, A S Semeikin *Zh. Org. Khim.* **29** 2445 (1993) [a]
87. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Struktura Konformerov Dimernykh Oktalkildifenilporfirinov s Mostikovymi Gruppami v o- i m-Polozheniyakh Benzol'nykh Fragmentov* (The Structure of Conformers of Dimeric β-Octaalkyldiphenylporphyrins with Bridging Groups in the *o*- and *p*-Positions of Benzene Fragments); article deposited at the VINITI No. 2941-V95 (Moscow, 1995)
88. N Zh Mamardashvili, S A Zdanovich, O A Golubchikov *Struktura Konformerov Dimernogo Oktalkilporfirina po Dannym Metoda Molekulyarnoi Mekhaniki* (The Structure of Conformers of Dimeric Octaalkylporphyrin From Molecular Mechanics Data); article deposited at the VINITI No. 2967-V95 (Moscow, 1995)
89. R Young, C K Chang *J. Am. Chem. Soc.* **107** 898 (1985)
90. A Lecas, J Levisalles, Z Renko, E Rose *Tetrahedron Lett.* **25** 1563 (1984)
91. T N Lomova, V V Morozov, E G Mozhzhukhina, B D Berezin, in *Spektroskopiya Koordinatsionnykh Soedinenii (Tez. Dokl. IV Vsesoyuz. Soveshch.), Krasnodar, 1986* [The Spectroscopy of Coordination Compounds (Abstracts of Reports of the IVth All-Union Meeting), Krasnodar, 1986] p. 264
92. T N Lomova, E G Mozhzhukhina, L P Shormanova, B D Berezin, in *V Vsesoyuz. Konf. po Koordinatsionnoi i Fizicheskoi Khimii Porfirinov (Tez. Dokl.), Ivanovo, 1988* [The Vth All-Union Conference on Coordination and Physical Chemistry of Porphyrins (Abstracts of Reports), Ivanovo, 1988] p. 64
93. N Datta-Gupta, T J Bardos *J. Heterocycl. Chem.* **3** 495 (1966)
94. C Kaldapa, J C Blais, V Carré, R Granet, V Sol, M Guilloton, M Spiro, P Krausz *Tetrahedron Lett.* **41** 331 (2000)
95. C K Chang *J. Heterocycl. Chem.* **14** 1285 (1977)
96. J A Cowan, J K M Sanders, G S Beddard, R J Harrison *J. Chem. Soc., Chem. Commun.* 55 (1987)
97. B M Trost, C R Hutchinson (Eds) *Organic Synthesis Today and Tomorrow* (Madison, WI: University of Wisconsin, 1980)
98. A Osuka, K Maruyama *J. Am. Chem. Soc.* **110** 4454 (1988)
99. C K Chang, I Abdalmuhdi *Angew. Chem.* **96** 154 (1984)
100. S S Eaton, G R Eaton, C K Chang *J. Am. Chem. Soc.* **107** 3177 (1985)
101. C K Chang, I Abdalmuhdi *J. Org. Chem.* **48** 5388 (1983)
102. J Weiser, H A Staab *Angew. Chem.* **96** 602 (1984)
103. H Ogoshi, H Sugimoto, Z-i Yoshida *Tetrahedron Lett.* 169 (1977)

104. J A Cowan, J K M Sanders *J. Chem. Soc., Chem. Commun.* 1213 (1985)
105. N E Kagan, D Mauzerall, R B Merrifield *J. Am. Chem. Soc.* **99** 5484 (1977)

[a] — *Russ. J. Org. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[c] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[d] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[e] — *Chem. Heterocycl. Compd. (Engl. Transl.)*