Synthesis and electronic spectra of dimeric phthalocyanines

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Dimeric phthalocyanines of a new type with a bridging 9,9,10,10-tetramethyl-9,10dihydroanthracene fragment were synthesized. On the basis of X-ray diffraction analysis and molecular modeling of 9,9,10,10-tetramethyl-9,10-dihydroanthracene, a nearly planar structure was assumed for these phthalocyanines. The electronic absorption spectra of the obtained phthalocyanines and their monomeric and conjugated dimeric analogs were compared.

Key words: phthalocyanines, exciton interaction, electronic spectra.

In recent years the interest in the synthesis and study of porphyrin oligomers as potential molecular conductors, nonlinear optical materials, and systems that simulate photosynthesis has markedly increased.¹ The oligomers of phthalocyanines, the most well-known porphyrin analogs, remain much less studied. Phthalocyanines have been extensively used for many years as dyes and pigments,² catalysts and photocatalysts,³⁻⁵ photoconductors in xerography,⁶ and photosensitizers in photodynamic tumor therapy.⁷ The enhanced attention to new phthalocyanine systems is due to a number of interesting properties such as conduction in a broad range,⁸ electrochromism,⁹ and mesogenic¹⁰ and nonlinear optical¹¹ properties most of which are due to specific features of the aromatic π -system of the phthalocvanine macrocycle. which is also responsible for exceptional thermal and chemical stabilities of these compounds. A possible way of modification of the electronic structures of conjugated systems is to extend the conjugation system. For phthalocyanines, this may be attained by fusing additional benzene rings at the macrocycle periphery¹² and by constructing conjugated oligomers.¹³ The former approach results in a pronounced decrease in the stability, whereas the conjugated systems of types 1 and 2 incorporating two phthalocyanine fragments, which we obtained previously,¹⁴ are rather stable.

The extension of the system of conjugation is typically accompanied by color deepening. In solutions, most phthalocyanines exhibit a strong absorption band around 680 nm (Q band), which shifts to the near IR region (840 nm) on going to dimers 1 and $2.^{14}$ The exciton interaction in nonconjugated dimers^{13,15–17} and in phthalo-

cyanine aggregates^{18–20} or crystals²¹ also induces shifts in electronic absorption bands depending on the mutual arrangement of macrocycles. The design of di- and oligomeric structures with various types of interaction of π -systems is of interest as a way of modification of the electronic properties of phthalocyanines with outlook to prepare new molecular materials. Quite a few nonconjugated phthalocyanine dimers with relatively flexible connecting units (bridges) in which one cannot determine with confidence the mutual positions of the macrocycles are known.^{13,15,16} The hypsochromic shift of the Q band is indicative of the predominant "face-to-face" orientation, which is also typical of aggregates in solutions,^{18,20} crystals,²¹ and liquid crystals¹⁰ of phthalocyanines. There exist dimers with more rigid bridges, which secure the phthalocyanine fragments in the "face-to-face" position¹⁶ and at an angle of ~ 100° .¹⁷ To our knowledge, nonconjugated dimers with "edge-to-edge" orientation of phthalocyanine fragments at an angle of 180° have not yet been prepared. These dimers are of interest as nonconjugated analogs of type 1 and 2 diphthalocyanines with purely exciton type of interaction of the Pc chromophores, which can be used to estimate the contribution of the conjugation to the change in the excitation energy compared to the monomeric analog and to study the effect of the mutual orientation of the chromophores on the photophysical properties of oligomeric structures. According to the exciton interaction theory,²² these should exhibit a red shift of the absorption bands in the electronic spectrum. Dimeric phthalocyanines obtained in this study contain a 9,9,10,10-tetramethyl-9,10-dihydroanthracene fragment connecting the macrocycles.

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 $R = 2,6-Me_2C_6H_3$

Results and Discussion

Phthalocyanine dimers were synthesized according to Scheme 1. The reductive methylation of anthracene by a known procedure afforded 9,9,10,10-tetramethyl-9,10dihydroanthracene $(3)^{23}$ whose tetracyano derivative was prepared in two steps via the intermediate 2,3,6,7-tetraiodo-9,9,10,10-tetramethyl-9,10-dihydroanthracene (4) by analogy with the procedure described previously²⁴ for a fenestrindane derivative. The yield of product 5 was 17% based on anthracene. A mixture of tetracyano derivative 5 with excess 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (6) was heated in *n*-butanol in the presence of a base (magnesium butoxide or DBU). For the synthesis of zinc phthalocyanines, zinc acetate was also added. Metal-free phthalocyanines were prepared by demetallation of magnesium phthalocyanines with trifluoroacetic acid. Mixed condensation gave a mixture of phthalocyanines, mainly, monomers 7 and 9 and dimers 8 and 10. Chromatography of the obtained mixtures on silica gel with gradient elution by toluene-ether (Zn phthalocyanines) or toluene—hexane (metal-free phthalocyanines) afforded monomers 7 and 9 and dimers 8 and 10. The yields of compounds 8 and 10 were 0.3 and 2.0%, respectively. Note that dimeric phthalocyanine 2 was prepared in 71% yield by standard metallation of monomer 1 with zinc acetate in a toluene—DMF mixture.¹⁴ A solubility of the resulting phthalocyanines sufficient for chromatographic separation and for the subsequent study is provided by the bulky 2,6-dimethylphenoxyl substituents R.

All compounds prepared in this work were characterized by electrospray ionization (ESI) mass spectrometry. Molecular or pseudomolecular ions without pronounced fragmentation were present in all cases.

The ¹H NMR data are summarized in Table 1. The shielding/deshielding effects typical of phthalocyanines caused by the ring current of the phthalocyanine aromatic π -system, which induced significant shifts of the proton signals depending on the proton position with respect to the macrocycle, are even more pronounced in phthalocyanine dimers of type 1,¹⁴ where the shifts of the signals are determined by two macrocycles. The protons located



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more closely to the center of the system are deshielded to a greater extent. This effect promotes signal resolution in the spectrum. The greatest chemical shifts are observed for the signals of the benzene type phthalocyanine protons, especially for the bridging benzene rings ($\delta > 11$ (1, 2) and ~9.5 (8, 10)). The broad signals of the methyl protons of the bridge in compounds 8 and 10 ($\delta ~3$) are also considerably shifted downfield compared to compound 3 (δ 1.65). Generally, the signals of dimers 8 and 10 are somewhat broadened compared to the signals of dimers 1 and **2**, which is apparently due to less rigid structure. The positions of signals for the internal pyrrole protons $(\delta \ 0 - -1)$ are due to the influence of the adjacent macrocycle, which decreases shielding, as opposed to dimeric phthalocyanines of the "face-to-face" type in which further upfield shifts are observed for these protons (up to $\delta - 8$).²⁰

It was shown by X-ray diffraction that compound 3 (Fig. 1, Table 2) is planar. The average deviation of the carbon atoms of the anthracene fragment from the plane



Scheme 1

 $R = 2,6-Me_2C_6H_3$

Table 1. ¹H NMR spectra of phthalocyanines 1, 2, 7–10

Compound	δ					
(solvent)	phthalocyanine	R		bridge H	pyrrole H	
	H arom.	H arom.	Me			
1 (CDCl ₃) ¹⁴	11.14 (s, 2 H); 9.06, 8.29, 8.15	7.32—7.44 (br.s, 36 H)	2.62, 2.48, 2.38 (all s, 24 H each)	_	-0.04 (br.s, 4 H)	
2 (C ₆ D ₆ , 60 °C)	(an s, 4 H each) 11.67 (s, 2 H); 9.69 (s, 4 H); 8.67–8.72	7.25—7.49 (br.s, 36 H)	2.66, 2.37, 2.29 (all s, 24 H each)	_	_	
7 (CDCl ₃) ¹⁴	(br.s, 8 H) 8.18 (s, 8 H)	7.30—7.41 (br.s. 24 H)	2.43 (s, 48 H)	_	-0.76 (br.s, 2 H)	
8 (CDCl ₃)	9.66, 8.63, 8.34, 8.19 (all s. 4 H each)	7.33–7.62 (br.s, 36 H)	2.60 (s, 24 H); 2.45–2.56 (br.s. 48 H)	3.30—3.78 (br.s, 12 H)	-0.43 (br.s, 4 H)	
9 (CDCl ₃)	8.19 (s, 8 H)	7.30—7.41 (br.s. 24 H)	2.43 (s, 48 H)	—	—	
10 (DMSO-d ₆ + KCN**)	9.49, 8.38, 7.93, 7.88 (all s, 4 H each)	7.45—7.73 (br.s, 36 H)	2.30—2.45 (br.s, 48 H)*	3.00 (br.s)*	_	

* A part of the signal is covered by the band of the residual DMSO-d₆ (δ 2.50) or water (δ 3.33) protons. ** ~10 mmol L⁻¹.

is 0.008 Å. Apparently, the 9,10-dihydroanthracene fragment in compounds **8** and **10** is also planar.

Table 2. Selected geometric parameters (bond lengths (d) and bond angles (ω)) of compound 3

Bond	d/Å	Angle	ω/deg
C(5)-C(6)	1.397(2)	C(5)-C(6)-C(7)	123.5(1)
C(6)-C(7)	1.526(2)	C(6)-C(7)-C(5A)	113.00(9)
C(7)-C(8)	1.545(2)	C(8)-C(7)-C(9)	109.16(9)



Fig. 1. Crystal structure of compound 3.

Obviously, the deviation from the planar structure gives rise to steric hindrance as the Me groups approach each other and the hydrogen atoms in positions 1, 4, 5, and 8. An analog of compound 3, 9,9,10,10-tetrachloro-9,10dihydroanthracene, also has a planar structure,²⁵ whereas unsubstituted 9,10-dihydroanthracene exists in a boat conformation with a dihedral angle between the benzene rings of 145°.²⁶ The molecular modeling of compound 3 (MM+ molecular mechanics method) also predicts a planar geometry. A deviation from the plane by rotation of one benzene ring through 30° around the C(7)–C(7A) axis followed by partial geometry optimization (with fixed coordinates of the carbon atoms of the benzene rings) entails an increase in energy by 25 kJ mol⁻¹. The fraction of molecules with an energy of ≥ 25 kJ mol⁻¹ per degree of freedom at 298 K is 0.004%, which suggests an essentially planar conformation of the bridge and dimers 8 and 10 as a whole.

The electronic absorption spectra of the dimeric phthalocyanine 1 in comparison with those of monomer 7 have been analyzed in detail previously.¹⁴ The spectra of compounds 2, 9, and 10 in THF are presented in Fig. 2 and those of compounds 7 and 8 in chloroform are in Fig. 3. As in the case of dimer 1,¹⁴ the long-wavelength absorption band of dimer 2 is shifted bathochromically by \sim 150 nm with respect to the monomeric analog, the extinction coefficient for compound 1 or 2 is higher than that for 7 or 9 but less than twice higher. Apart from the band at about 850 nm, the spectrum exhibits a number of low-intensity bands in the range of 500-800 nm associated with the higher excited states of the dimeric system and with the vibronic components of the long-wavelength band. Unlike these significant changes in the spectrum taking place on going from monomeric phthalocyanines 7 and 9 to conjugated dimers 1 and 2, the electronic spectra of dimers 8 and 10 almost do not differ from the spectra of monomers 7 and 9 (Table 3): only a slight red shift of the



Fig. 2. Electronic spectra of phthalocyanines 2 (1), 9 (2) and 10 (3) in THF ($\times 0.5$ (1, 3)).



Fig. 3. Electronic spectra of phthalocyanines 7 (1) and 8 ($2, \times 0.5$) in chloroform.

Q band is observed, and in the case of metal-free phthalocyanines, minor differences between the Soret bands (300–450 nm) can be noted. The extinction coefficients for compounds 8 and 10 are almost twice as high as those for compounds 7 and 9. Hence, in this case, the phthalocyanine fragments behave as almost independent chromophores, unlike those in conjugated dimers 1 and 2. Nonconjugated phthalocyanine dimers of the "face-toface" type^{15,16} and aggregates^{18,20} tend to exhibit a fairly broad absorption band at about 630 nm, which is shifted hypsochromically compared to that for monomer analogs by ~50 nm. The relatively weak interaction of the phthalocyanine chromophores in dimers 8 and 10 can be attributed to considerably weaker overlap of the π -orbitals compared to the "face-to-face" dimers.

Thus, we prepared new-type phthalocyanine dimers with the 9,9,10,10-tetramethyl-9,10-dihydroanthracene bridge, presumably having a planar structure (based on X-ray diffraction data for the bridging fragment 3). These compounds are nonconjugated analogs of type 1 and 2 dimers. The electronic spectra of dimers 8 and 10 indicate

Table 3. Electronic spectra of phthalocyanines 2, 7–10

Com- pound	$\lambda_{\rm max}/{\rm nm}~(\epsilon \cdot 10^{-5})$				
	Q band	Soret band			
2	840 (4.70), 794 (0.61),	363 (1.87)			
	748 (0.93), 722 (1.08)				
7	704 (1.65), 667 (1.39),	420 (0.41),			
	648 (0.47), 605 (0.28)	350 (0.86)			
8	708 (3.22), 675 (2.57),	394 (0.72),			
	654 (0.93), 611 (0.50)	349 (1.57)			
9	674 (3.38), 644 (0,42),	355 (1.06)			
	608 (0.47)				
10	682 (6.9), 652 (0.85),	356 (2.2)			
	615 (0.83)				

the absence of exciton interaction between the phthalocyanine chromophores, which attests to a crucial role of conjugation in their interaction in dimers 1 and 2. Weaker interaction compared to that in the "face-to-face" type dimers may be due to insignificant overlap of the macrocycle π -orbitals.

Experimental

IR spectra were recorded on a Perkin–Elmer Spectrum 1000 spectrometer for KBr pellets, the electronic spectra were measured on a Perkin–Elmer Lambda 25 spectrometer, and NMR spectra were obtained on a Bruker Avance DPX 200 instrument (200 MHz (¹H); CDCl₃, acetone-d₆, and DMSO-d₆ as solvents; sample concentrations <1 mmol L⁻¹; the chemical shifts were referred to Me₄Si based on the residual proton signals of the solvent). EI mass spectra (70 eV) were recorded on a Finnigan MAT 95 mass spectrometer and ESI mass spectra were run on a Bruker Esquire LC instrument.

Commercial solvents (Fluka, analytically pure grade) were used as received for recording the spectra and dried by standard methods for the syntheses. Column chromatography was carried out using silica gel 60 (Merck) with a particle size of 40–63 μ m. Sulfuric acid, periodic acid, potassium iodide, copper(1) cyanide, DBU, magnesium turnings, and trifluoroacetic acid (Fluka) were used as received. Zinc acetate dihydrate (Fluka) was dried *in vacuo* at 110 °C over P₂O₅ (drying is accompanied by partial hydrolysis, which is not important in this case). 9,9,10,10-Tetramethyl-9,10-dihydroanthracene (**3**),²³ 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (**6**), and phthalocyanines **1** and **7** were synthesized using previously described procedures.¹⁴

Zinc complex of 2,3,7,8,12,13,19,20,24,25,29,30-dodeca(2,6-dimethylphenyloxy)tribenzo[b,g,l]-21H,23H-5,10,15,20-tetraazaporphyno[2,3-b]-29H,31H-phthalocyanine (2). A solution of zinc acetate dihydrate (44 mg, 0.2 mmol) in DMF (1 mL) was added to a solution of compound 1 (24 mg, 10 µmol) in toluene (2 mL). The mixture was refluxed for 15 h, cooled, and diluted with methanol (10 mL). The resulting precipitate was separated by centrifugation, washed with methanol, dried, and dissolved in toluene. The solution was chromatographed on silica gel with a toluene-ether mixture as the eluent (8% ether v/v). A blue violet fraction was collected, the solvents were evaporated under reduced pressure, and the residue was reprecipitated by hexane from toluene and dried *in vacuo* at 60 °C. Yield 18 mg (71%), a black powder. Found (%): C, 73.05; H, 4.86; N, 9.13. C₁₅₄H₁₂₂N₁₆O₁₂Zn₂. Calculated (%): C, 73.41; H, 4.88; N, 8.89. MS ESI (CH₂Cl₂-DMF (1 : 10), positive ion mode), m/z: 1258 [M + 2 H]²⁺.

2,3,6,7-Tetraiodo-9,9,10,10-tetramethyl-9,10-dihydroanthracene (4). Periodic acid (H_5IO_6) (1.09 g, 4.8 mmol) was dissolved in conc. H_2SO_4 (48 mL) at 0 °C, and KI (2.39 g, 14.4 mmol) was added with stirring in small portions. Compound **3** (0.28 g, 1.2 mmol) was added to the resulting solution, cooling was terminated, and the solution was stirred for 14 h. The mixture was poured into ice water, and the precipitate was filtered off, washed with water and methanol, dried, dissolved in chloroform, and passed through a short column with silica gel. The solvent was evaporated, and the precipitate was washed with methanol and dried *in vacuo*. Yield 0.42 g (48%), a pinkish powder. Found (%): C, 29.38; H, 1.93. C₁₈H₁₆I₄. Calculated (%): C, 29.22; H, 2.18. ¹H NMR (DMSO-d₆), δ : 8.01 (s, 4 H); 1.53 (s, 12 H). MS (EI, 70 eV), m/z (I_{rel} (%)): 740 [M]⁺ (31), 725 [M - CH₃]⁺ (100), 710 [M - 2 CH₃]⁺ (20), 598 [M - CH₃ - I]⁺ (11), 471 [M - CH₃ - 2 I]⁺ (12), 456 [M - 2 CH₃ - 2 I]⁺ (15), 329 [M - 2 CH₃ - 3 I]⁺ (7), 299 [M - CH₃ - I]²⁺ (10), 243 [M - 2 I]²⁺ (11), 202 [M - 2 CH₃ - 4 I]⁺ (20), 101 [M - 2 CH₃ - 4 I]²⁺ (25).

9,9,10,10-Tetramethyl-9,10-dihydroanthracene-2,3,6,7tetracarbonitrile (5). A mixture of compound 4 (1.85 g, 2.5 mmol) and CuCN (9.90 g, 110 mmol) in pyridine (0.5 L) was heated for 20 h at 115 °C, concentrated to a small volume, and diluted with excess 25% aq. ammonia. The precipitate was washed with 25% aq. ammonia and water, dried, and extracted with acetone, the solution was concentrated, and the residue was extracted again with acetone. The extract was passed through a short column with silica gel and concentrated, and the residue was washed with methanol and dried *in vacuo*. Yield 0.50 g (59%), colorless crystals. Found (%): C, 78.22; H, 4.64; N, 16.94. $C_{22}H_{16}N_4$. Calculated (%): C, 78.55; H, 4.79; N, 16.66. IR (KBr), v/cm^{-1} : 2229 (C=N). ¹H NMR (acetone-d₆), δ : 8.45 (s, 4 H); 1.86 (s, 12 H). MS (EI, 70 eV), m/z (I_{rel} (%)): 336 [M]⁺ (2), 321 $[M - CH_3]^+$ (100), 306 $[M - 2 CH_3]^+$ (36), 291 $[M - 3 CH_3]^+$ (10).

2,3,9,10,16,17,37,38,42,43,47,48-Dodeca(2,6-dimethylphenyloxy)-33,33,66,66-tetramethyl-33,66-dihydrobenzo[1,2-b;3,4-b[']]-29H,31H-bisphthalocyanine (8). Magnesium turnings (0.15 g) were dissolved in boiling butanol (40 mL) $(\sim 2 h)$. The resulting suspension was cooled, and compound 5 (0.17 g, 0.5 mmol) and compound 6 (1.47 g, 4 mmol) were added. The mixture was refluxed for 48 h, cooled, and diluted with methanol (200 mL). The precipitate formed was separated by centrifugation, washed with methanol, dried, and extracted with toluene. Toluene was evaporated under reduced pressure, and the residue was dissolved in CF₃COOH (25 mL). The solution was stirred in the dark for 1 h at ~20 °C and poured in ice water (~100 mL). The precipitate was separated by centrifugation, washed with water, a 5% solution of NaHCO₃ and again water, dried, and extracted with a toluene-hexane mixture (15% hexane, v/v). The solution of a phthalocyanine mixture thus formed was chromatographed on silica gel with a toluene-hexane mixture as the eluent (the hexane content was gradually decreased from 15 to 5%). The second fraction was collected, the solvent was removed under reduced pressure, and the residue was recrystallized from toluene and dried in vacuo at 60 °C. Yield 3.7 mg (0.3%), green flakes. Found (%): C, 78.08; H, 5.82; N, 8.48. C₁₆₆H₁₄₀N₁₆O₁₂. Calculated (%): C, 78.16; H, 5.53, N, 8.79. IR (KBr), v/cm⁻¹: 3305 (N-H). ESI MS (CH₂Cl₂-pyridine (1 : 100), negative ion mode), *m/z*: 2548 [M]⁻.

Zinc complex of 2,3,9,10,16,17,23,24-octa(2,6-dimethylphenyloxy)-29H,31H-phthalocyanine (9) and zinc complex of 2,3,9,10,16,17,37,38,42,43,47,48-dodeca(2,6-dimethylphenyloxy)-33,33,66,66-tetramethyl-33,66-dihydrobenzo[1,2-b;3,4-b']-29H,31H-bisphthalocyanine (10). A mixture of compound 5 (55 mg, 0.16 mmol), compound 6 (0.6 g, 1.6 mmol), zinc acetate (70 mg), and DBU (0.4 mL) in *n*-butanol (4 mL) was refluxed for 15 h, cooled, and diluted with methanol (20 mL). The resulting precipitate was separated by centrifugation, washed with methanol, dried, extracted with toluene, and chromatographed on silica gel with a toluene—ether mixture as the eluent, the ether content being gradually increased to 9%. The first and second fractions containing products 9 and 10, respectively, were collected. The solvent was removed under reduced pressure and the compound was recrystallized from toluene and dried *in vacuo* at 60 °C. <u>Compound 9</u>. Yield 0.27 g (43%), green flakes. Found (%): C, 75.14; H, 5.31; N, 7.29. C₉₆H₈₀N₈O₈Zn. Calculated (%): C, 74.92; H, 5.24; N, 7.28. ESI MS (CH₂Cl₂—MeOH (1 : 10), negative ion mode), *m/z*: 1571 [M + Cl]⁻. <u>Compound 10</u>. Yield 9.0 mg (2.0%), green flakes. Found (%): C, 74.07; H, 5.09; N, 8.51. C₁₆₆H₁₃₆N₁₆O₁₂Zn₂. Calculated (%): C, 74.45; H, 5.12; N, 8.37. MS ESI (DMF + NaCN (~1 mmol L⁻¹), negative ion mode), *m/z*: 1362 [M + 2 CN]^{2–}.

X-Ray diffraction analysis of compound 3. The crystals were prepared by slow evaporation of an acetone solution. X-Ray diffraction data were collected at 100 K on a Bruker AXS SMART APEX diffractometer (ϕ - ω scanning, Mo-K α radiation, λ = 0.71073 Å, graphite monochromator). Absorption corrections were applied using the SADABS program.²⁷ The structure was solved by the direct method using the SHELXS97 software ²⁸ and refined by the full-matrix least squares method on F^2 using the SHELXL97 software.²⁹ All nonhyrogen atoms were refined in the anisotropic approximation. The hydrogen atoms were found from the difference electron density synthesis and refined isotropically. Crystal data and X-ray diffraction experiment details: $C_{18}H_{20}$, M = 236.34, orthorhombic system, space group *Pbca*, a = 11.3901(10) Å, b = 8.0274(7) Å, c =14.5761(13) Å, $\alpha = 90^{\circ}$, V = 1332.7(2) Å³, Z = 4, $d_{calc} =$ 1.178 g cm⁻³, $\mu = 0.66$ cm⁻¹, the range of θ was 2.79–26.50°, the number of measured reflections was 7597, the number of independent reflections (R_{int}) was 1370 (0.03), the number of refined parameters was 123, F(000) = 512, $R_1(I \ge 2\sigma(I)) = 0.04$, wR_2 (for all reflections) 0.1198, $S(F^2) = 0.941$.

The geometry of compound 3 was optimized and the strain energies were calculated by the MM+ method using the HyperChem 5.02 software.³⁰ The electrostatic interactions were calculated from the bond dipole moments.

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