Notiz / Note

Unsymmetrical Phthalocyanines with a Single Macrocyclic Substituent

Emel Musluoglu[a], Aysegül Gürek[a], Vefa Ahsen[a], Ahmet Gül[a,b], and Özer Bekaroğlu*[a,b]

Department of Chemistry, TUBITAK Marmara Research Center[a],
P. O. Box 21, 41470 Gebze, Kocaeli, Turkey

Department of Chemistry, Technical University of Istanbul[b],
Maslak, Istanbul, Turkey

Received April 24, 1992

Key Words: Phthalocyanines, unsymmetrical / Crown ethers / Monoaza crown ethers / Tetraaza macrocycles

Unsymmetrical phthalocanines (**5**–**7**) with a single macrocyclic substituent are synthesized by the reaction of the boron complex of phthalonitrile (**1**) with the iminoisoindoline derivatives **2**–**4** of macrocyclic compounds, i.e. 15-crown-5, monoaza-15-crown-5, and tetraazacyclotetradecane. The monomacrocycle-substituted phthalocyanines are less soluble than the tetra-substituted one.

Phthalocyanines and their symmetrically substituted derivatives have received extensive interest in the last decades since their special properties (e.g. electrical conductivity[1], electrochromism[2], mesophase formation[3], photosensitivity[4]), makes them interesting substrates for novel materials[5]. In contrast, little is known about the unsymmetrical derivatives of phthalocyanines which are expected to maintain additional facilities in areas like nonlinear optics[6] and photodynamic therapy[7]. The reason for the limited interest in these types of compounds is mainly attributed to the difficulty of isolating the desired product from the statistical condensation of two or more different phthalonitrile derivatives. Consequently, the synthetic route employing subphthalocyanines which can be considered a template reaction is extremely advantageous[8,9].

The strategy preferred in this work makes use of the preorganization of three phthalodinitrile units in the form of a B^{III} complex which is subsequently converted into unsymmetrical phthalocyanines by reaction with various substituted iminoisoindolines[8,9]. The macrocyclic groups were chosen as the substituents for the unsymmetrical molecule, since the phthalocyanines carrying four of these groups symmetrically have been shown to be soluble in common organic solvents to a considerable degree and capable of binding various metal ions[10–15].

Results and Discussion

The precursor boron complex **1** was easily obtained by treatment of BCl_3 or BBr_3 with phthalonitrile as described[9,16,17]. The high affinity of B^{III} to ether and aza groups prevented the preparation of boron complexes from the substituted phthalodinitrile derivatives.

The reaction of **1** with the iminoisoindoline derivatives **2**–**4** containing a macrocycle yields the unsymmetrical phthalocyanines **5**–**7** with only one macrocycle. Compared to this possibility of a 3 + 1 combination of phthalonitrile with its substituted derivative other combinations are unlikely, based on a number of pieces of evidence: i) the boron complex binds the first three phthalonitrile molecules at the beginning, and insertion of the fourth component occurs in the second step; ii) in all three examples (**5**–**7**), elemental analyses indicate a 3 + 1 combination of the two components, and the presence of a single product is demonstrated by TLC in each case; iii) TGA results confirm a decomposition at ca. 400°C of a single macrocycle group for each phthalocyanine molecule as the first step with the decomposition of the core of the molecule occurring afterwards.

The phthalocyanines **5**–**7** were precipitated from the α-chloronaphthalene/DMSO medium by the addition of water and isolated by simple filtration as analytically pure products after drying. As anticipated, the products show a rather low solubility in organic solvents when compared with the tetrasubstituted phthalocyanines carrying similar macrocycles. Only **7** is sufficiently soluble in $CDCl_3/CD_3OD$ to allow recording of its NMR spectrum. This spectrum clearly exhibits the peripherally unsubstituted aromatic groups (δ = 8.26–7.80) along with the signals corresponding to the protons in the tetraaza macrocycle (δ = 2.99–2.66). Also the typical strongly shielded cavity hydrogen atoms are observed as broad signals at δ ca. −4.20. In the IR spectra of these phthalocyanines, the cavity NH stretching vibrations are observed at ca. 3300 cm^{-1}. Also the characteristic absorption of each macrocycle are in agreement with the reported IR spectra of similar compounds[10–14].

The alkali ion binding property of crown ethers containing phthalocyanine **5** was verified by the formation of the **5** · NaSCN adduct the IR spectrum of which in ethanol exhibits a characteristic SCN^- vibration at 2050 cm^{-1}. However, the enhancement of solubility as a result of adduct formation is almost negligible. In the case of the *N*-acetylmonoaza-15-crown-5-substituted phthalocyanine deacetylation was accomplished by hydrolysis in 1.2 M HCl at reflux temperature for 14 h, but quaternarization with dimethyl sulfate even under extreme conditions did not give the desired product. This is in clear contrast with the (tetramonoazacrown ether)-substituted phthalocanine which can be simultaneously deacetylated and quaternarized in chloroform/dimethyl sulfate mixtures[12b].

The visible absorption spectral data are given in Table 3 along with those of symmetrically tetrasubstituted counterparts. The splitting pattern of the Q bands around 680 nm is very similar in both symmetrical and unsymmetrical derivatives. The loss of symmetry appears to cause no appreciable splitting. In contrast to the unsym-

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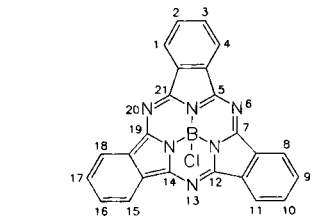
metrical (18-crown-6)-linked dinuclear phthalocyanines where the absorption coefficients in the Q band are intensier than those in the Soret region[18]. A just opposite relationship is observed for the phthalocyanines **5**–**7** and their symmetric counterparts[10,12]. Also, the shift of Q bands as a function of different macrocycles (e.g. all-oxa, tetraoxamonoaza, and tetraaza) on the periphery is relatively small.



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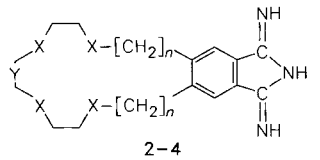
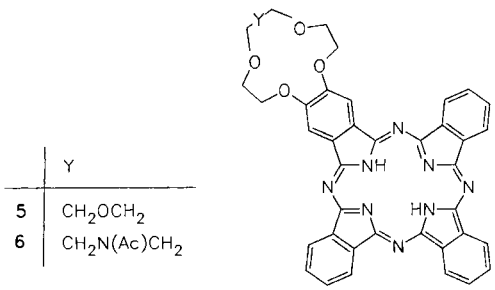


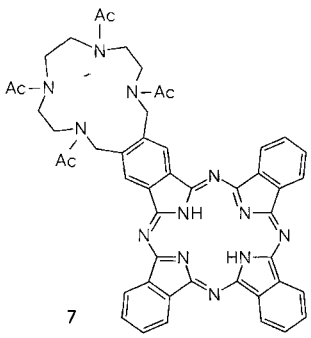
2–4

→ Unsymmetrical Phthalocyanines

	X	Y	n
2	O	CH_2OCH_2	0
3	O	$CH_2N(Ac)CH_2$	0
4	NAc		1



	Y
5	CH_2OCH_2
6	$CH_2N(Ac)CH_2$



7

Experimental

Chloro[7,12 : 14,19-diimino-21,5-nitrilo-5*H*-tribenzo-[*c*,*h*,*m*][1,6,11]triazacyclopentadecinato(2−)-N^{22},N^{23},N^{24}]-(T-4)-boron (**1**)[9,16], 7-Acetyl-15,16-dicyano-2,3,5,6,8,9,11,12-octahydro-5*H*-benzo[*e*][1,4,7,10,13]tetraoxazacyclopentadecine[12], 2,3,5,6,8,9,11,12,16,17-decahydro-15,17-diimino-15*H*-isoindolo[5,6-*b*][1,4,7,10,13]pentaoxacyclopentadecine[11] (**2**) and 2,5,8,11-tetra-acetyl-3,4,6,7,9,10,12,14,15,16-decahydro-14,16-diimino-1*H*-isoindolo[5,6-*l*][1,4,7,10]tetraazacyclotetradecine[14,19] (**4**) were prepared according to literature procedures.

IR (KBr) (Table 1): Perkin Elmer-983 Spectrophotometer. — UV/Vis (Table 2): Varian DMS 90. — Elemental analyses (Table 3): Instrumental Analytical Laboratory of TUBITAK Gebze Research Center. — Thermogravimetric analyses: Du Pont differential thermoinstrument (type 990), 10°C min^{-1}, nitrogen flow (100 cm^3 min^{-1}). — ^1H NMR: Bruker (200 MHz).

Table 1. Characteristic IR bands [cm^{-1}] of unsymmetrical phthalocyanines (KBr pellets)

	ν_{NH}	ν_{CH_2}	$\nu_{C=O}$	$\nu_{C-O-C_{arom}}$	ν_{C-O-C}
5	3300	2940	—	1280–1205	1100–1010
6	3300	2940	1640	1280–1210	1130–1010
7	3300	2920	1640	—	1220–1120

Table 2. UV/Vis data for the symmetrical and unsymmetrical phthalocyanines in chloroform

Compound	λ/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})				
5[a]	680 (3.3)	650 (3.22)	617 (1.52)	590 (1.1)	325 (2.12)
5a[10]	701 (12.61)	661 (10.34)	644 (4.53)	601 (2.4)	348 (7.51)
6[a]	682 (4.08)	659 (3.9)	612 (2.8)	590 (1.48)	320 (2.92)
6a[12]	697 (19.84)	659 (15.8)	600 (3.5)	—	344 (11.4)
7	680 (11.5)	647 (12.02)	620 (4.26)	591 (2.74)	327 (7.3)

[a] In DMSO. — **5a**: Tetra(15-crown-5)phthalocyanine, **6a**: Tetra(*N*-acetylmonoaza-15-crown-5)phthalocyanine.

Table 3. Elemental analyses and thermogravimetric results of the phthalocyanines

Compound	Formula (Mol. mass)	Analysis Calcd. (Found) C	H	N	Mass loss[a] Calcd./Found
3	$C_{18}H_{24}N_4O_5$ (376.4)	57.43 (57.65)	6.42 (6.72)	14.88 (14.65)	
5	$C_{40}H_{32}N_8O_5$ (704.7)	68.17 (68.06)	4.57 (4.51)	15.90 (14.50)	27.3/28.0
6	$C_{42}H_{35}N_9O_5$ (745.8)	67.64 (67.36)	4.73 (4.56)	16.90 (16.54)	31.3/31.8
7	$C_{48}H_{44}N_{12}O_4$ (853.0)	67.59 (67.68)	5.20 (5.36)	19.71 (19.96)	39.9/40.1

[a] Weight loss corresponding to the breakdown of single macrocyclic substituents.

7-Acetyl-2,3,5,6,8,9,11,12,16,17-decahydro-15,17-diimino-15H-isoindolo[5,6-e][1,4,7,10,13]tetraoxazacyclopentadecine (**3**): 7-Acetyl-15,16-dicyano-2,3,5,6,8,9,11,12-octahydro-5*H*-benzo-[*e*][1,4,7,10,13]tetraoxazacyclopentadecine (1.52 g, 4.23 mmol) was dissolved in dry methanol (90 ml) under Ar, then sodium methoxide (0.114 g, 2.115 mmol) in dry methanol (10 ml) was added to the solution. Anhydrous ammonia was bubbled through the reaction mixture at room temp. for 3 h and then at reflux temp. for 12 h after which time the reaction was complete (TLC). The volume of the solution was reduced to 20 ml in vacuo and a yellowish-green product precipitated. Yield: 1.2 g (75%), m.p. 173–175°C (dec.). — ^1H NMR ([D_6]DMSO): δ = 8.36 (br, s, 3H), 7.45 (s, 2H), 4.12–3.36 (m, 16H), 2.01 (s, 3H). ^{13}C-decoupled: 170.04, 168.43, 150.44, 129.26, 105.41, 70.46, 69.29, 69.02, 68.86, 21.46.

Unsymmetrical Phthalocyanine **5**: A mixture of **1** (0.48 g, 1.115 mmol) and **2** (2.61 g, 7.78 mmol) was treated at 85–90°C in di-

methyl sulfoxide/1-chloronaphthalene (2:1, v/v) for 12 h. After cooling, the dark green product was precipitated with ethanol, filtered off, washed first with hot water, then with ethanol and dried with diethyl ether. Yield: 0.35 g (44.5%). Compound **5** was slightly soluble in DMF and DMSO.

Compound **6** was synthesized similar to **5** by starting with **3** (1.0 g, 2.65 mmol) and **1** (177 mg, 0.41 mmol). Yield of **6**: 0.20 g (65%). It was slightly soluble in DMF and DMSO.

Compound **7** was synthesized similar to **5** by starting with **4** (0.646 g, 1.34 mmol) and **1** (0.083 g, 0.193 mmol) at 130–140°C. The crude mixture was dissolved in chloroform (5 ml) and the solution filtered. To the filtrate diethyl ether was added. The blue precipitate was filtered off and dried with diethyl ether. Compound **7** was soluble in chloroform, DMSO and DMF. – ^{1}H NMR ($CDCl_3/CD_3OD$): δ = 8.26–7.80 (br, 14H, aromatic H), 4.04 (s, 4H, ar-CH_2N), 2.99–2.66 (m, 12H, CH_2), 2.19, 1.91 (s, 12H, CH_3CON), –4.20 (s, 2H, NH).

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