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Preparation of 1,2-bis(3,4-dicyanophenoxymethyl)benzene and the binuclear zinc phthalocyanine derived from it

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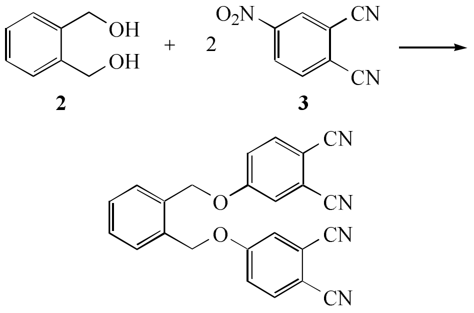
A method of synthesis of 1,2-bis(3,4-dicyanophenoxymethyl)benzene from the 1,2-bis(hydroxymethyl)benzene and 4-nitrophthalodinitrile is developed. Its tetramerization with $Zn(OAc)_2 \cdot 2H_2O$ gives a binuclear zinc phthalocyanine of a new type, containing four *o*-phenylidene bridges. The use of microwave heating decreases reaction time and increases yield.

The synthesis and study of binuclear phthalocyanines is one of the priorities of modern phthalocyanine chemistry. Due to interaction between phthalocyanine rings and a covalent bridge between them, binuclear phthalocyanines can have specific electro- and photocatalytic properties.[1,2]

Recently, the attention of investigators has been attracted to binuclear phthalocyanines linked by only one bridge, called as the clamshell.[2] At the same time, the synthesis and properties of binuclear phthalocyanines with a greater number of cross-links are not described in the literature.

In order to obtain a new type of binuclear phthalocyanine, we carried out the synthesis of 1,2-bis(3,4-dicyanophenoxymethyl)benzene **1** according to Scheme 1[†] by the common method[1] of nucleophilic substitution of an activated nitro group in an aromatic ring.



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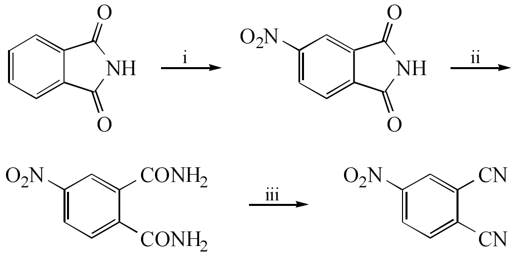
Scheme 1

1,2-Bis(hydroxymethyl)benzene **2** has been previously synthesised.[3] 4-Nitrophthalodinitrile **3** was obtained according to Scheme 2. To obtain 4-nitrophthalimide, we used NH_4NO_3 in concentrated H_2SO_4.[‡] Stages ii and iii were made by published methods,[4,5] respectively.



Scheme 2 *Reagents and conditions*: i, conc. H_2SO_4, NH_4NO_3, 0 °C; ii, NH_4OH, 20 °C; iii, $POCl_3$, Py, 0 °C.

There are published data on the synthesis and properties of binuclear phthalocyanines linked by one covalent bridge.[1–3] Such phthalocyanines were synthesised by the interaction of bisphthalodinitriles with a large excess of phthalodinitrile or the corresponding derivatives of *o*-phthalic acid. Under these conditions, a large amount of monophthalocyanine was obtained as a by-product.

To eliminate a possibility of the formation of phthalocyanines with a different structure, we used only one phthalodinitrile **1** for the formation of binuclear phthalocyanine (Scheme 3).[§] Phthalocyanine **4** was purified by TLC (Silufol UV-254, eluted with MeOH, then $CHCl_3$). It is readily soluble in the majority of organic solvents. In the electronic absorption spectrum (Figure 1), the Q-band occurs at 680 nm, characteristic of a D_{4h} symmetry, and the Sort-band at 352 nm. In the MALDI-TOF[¶] MS spectrum (Figure 2) there is a peak of the molecular ion 1692 (M^+, the molecular weight of phthalocyanine **4** is 1692.392). As a peak with *m*/*z* 846 is absent in the mass spectrum, we conclude that the side-strapped monophthalocyanine is not present.

Recently, we reported[6] on the synthesis of mono- and bisphthalocyanines under microwave irradiation. The application

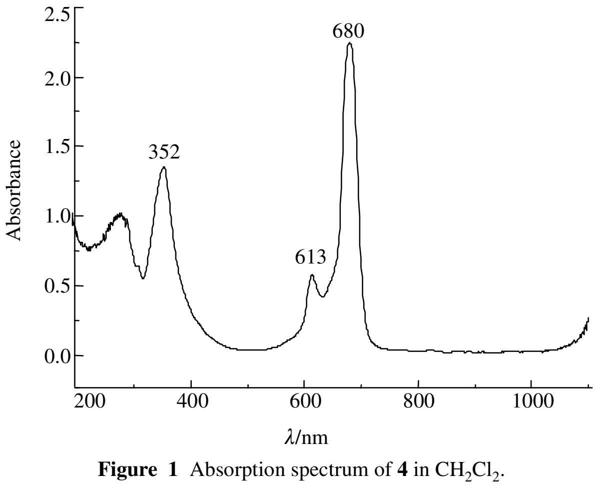


Figure 1 Absorption spectrum of **4** in CH_2Cl_2.

[†] *Reaction procedure*: A mixture of **2** (2.67 g, 0.019 mol), **3** (8 g, 0.046 mol) and K_2CO_3 (2 g) in 100 ml DMSO was intensively stirred for 15 h at 70 °C. After that, 2 g of K_2CO_3 was added and reaction was continued for 15 h at the same temperature. Reaction was monitored by TLC. Then the reaction mixture was poured into 500 ml of water, and acetic acid was added to the mixture. The residue was filtered off, flushed several times with water and recrystallised from EtOH. The reaction product was dried in air at 70 °C. 6.22 g (84%) of compound **1** was obtained. Mp 229 °C. ^{1}H NMR ($CDCl_3$) δ: 5.51 (d, 4H, CH_2, *J* 5 Hz), 7.4–8.1 (m, 10H, Ar). IR, ν_{max}/cm^{-1}: 1275 (m), 1020 (w), 3100 (w), 1250 (m), 780 (w), 1610 (w), 2224 (w). MS, *m*/*z*: 390 (M^+). Found (%): C, 73.61; 73.70; H, 3.65, 3.72; N, 14.40, 14.52. Calc. for $C_{96}H_{56}N_{16}O_8Zn_2$ (%): C, 73.85; H, 3.59; N, 14.35.

[‡] *Reaction procedure*: 28 g (0.19 mol) of phthalimide was added to 32 g (0.4 mol) of NH_4NO_3 in 400 ml H_2SO_4 (*d* 1.84). Reaction mixture was stirred for 2 h, then poured on ice (300 g). The product was filtered off and flushed with water until neutral. The substance was dried in air at 60 °C. After crystallization from ethanol, 22.5 g (58.6%) of pure 4-nitrophthalimide were obtained. Mp 200 °C (lit.,[4] mp 200–202 °C). IR, ν_{max}/cm^{-1}: 3340 (NH), 1710 (C=O).

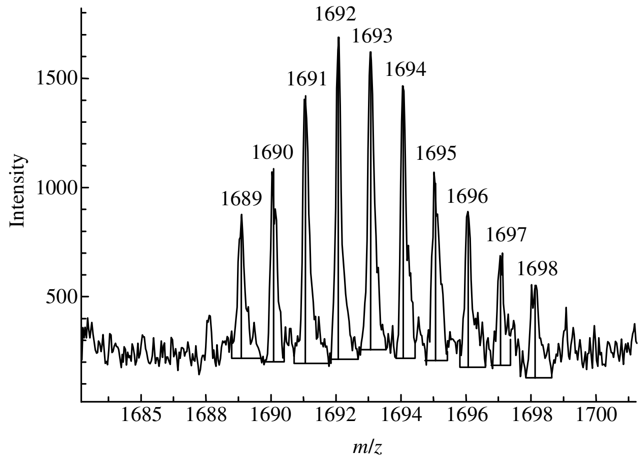


Figure 2 The molecular ion of **4**.

of microwave irradiation considerably simplified the synthesis, reducing the time of synthesis from several hours to several minutes. The synthesis of binuclear phthalocyanine **4** was carried out by irradiation of a homogeneous solution of compound **1** in *o*-DCB in the presence of two equivalents of $Zn(OAc)_2 \cdot 2H_2O$ in a microwave oven (Samsung, model M1915NR). The irradiation power varied from 100 to 400 W, time, from 5 to about 30 min. Experimentally, optimum conditions for the synthesis of binuclear phthalocyanine were found. On the one hand, the full conversion of bisphthalonitrile **1** took place, and, on the other hand, a smaller formation of by-products, resulting in the increased yield of the main product was observed. Thus, the optimum conditions for the microwave synthesis of **4** are as follows: irradiation power of 300 W and reaction time of 15 min. The yield of phthalocyanine was 6.8%. Thus, the use of microwave irradiation decreased the reaction time and increased the yield of the binuclear phthalocyanine.

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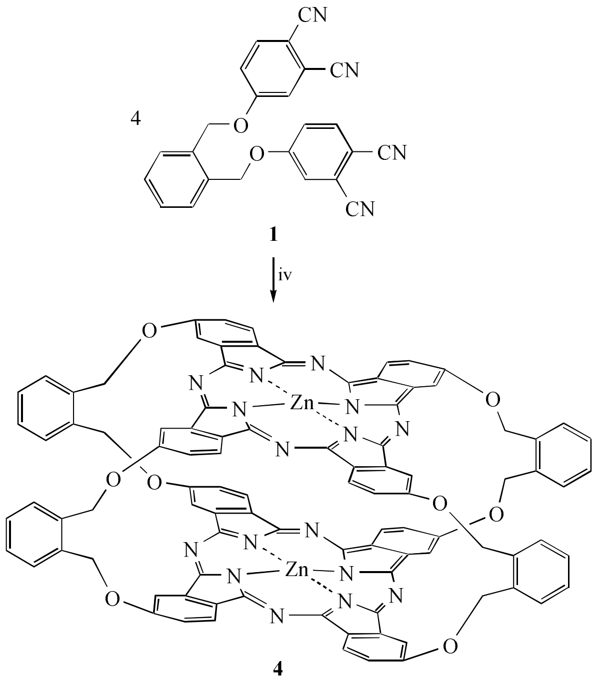

Scheme 3 *Reagents and conditions*: iv, DBU, isoamyl alcohol, $Zn(OAc)_2 \cdot 2H_2O$, *o*-DCB, 14 h, 180 °C.

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[§] *Reaction procedure*: 55 mg of $Zn(OAc)_2 \cdot 2H_2O$ (0.25 mmol), 0.5 ml of isoamyl alcohol and 0.3 ml of DBU were added to a solution of 0.2 g (0.5 mmol) of compound **1** in 25 ml of *o*-dichlorobenzene. The mixture was boiled in an atmosphere of argon for 14 h. After completion of the reaction, the reaction mixture was filtered, and the residue on the filter was repeatedly flushed with chloroform. The filtrate was evaporated and the greasy residue was multiply flushed at first with methanol and then with chloroform. The extracts were combined and evaporated to give binuclear phthalocyanine **4** (4 mg, 1.84%). ^{1}H NMR ($CDCl_3$) δ: 5.20 (m, 16H, OCH_2), 7.2–7.8 (m, 40H, Ar). UV–VIS (CH_2Cl_2, λ_{max}/nm): 352, 613, 680. MS, *m*/*z*: 1691 (M^+). Found (%): C, 68.42; 68.53; H, 3.12, 3.04; N, 13.60, 13.70. Calc. for $C_{96}H_{56}N_{16}O_8Zn_2$ (%): C, 68.13; H, 3.34; N, 13.24.

[¶] The sample was deposited on the matrix and analysed by an ionization method during laser desorption.