Symmetrical tetrasubstituted phthalocyanines containing condensed 2-alkylimidazole units

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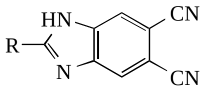
Symmetrical tetrasubstituted copper phthalocyanines with four condensed 2-alkylimidazole units have been synthesised and characterised.

One of the most important properties of substituted phthalocyanines is the ability to form Langmuir–Blodgett films. These films are of prime practical interest for the preparation of gas sensors[1] and materials for non-linear optics[2] and microelectronics.[3] Phthalocyanines containing both lipophilic and hydrophilic functional groups are very promising substances for these purposes.[4]

Various types of tetrasubstituted phthalocyanines are well known. However, little is known about symmetrical tetrasubstituted phthalocyanines.[5] In this work, we consider the use of 2-alkyl-5,6-dicyanobenzimidazoles as convenient precursors for the preparation of symmetrical tetrasubstituted copper phthalocyanines containing four condensed 2-alkylimidazole units.

The initial 2-alkyl-5,6-dicyanobenzimidazoles **2**–**4** were obtained in 61, 38 and 14% yields for **2**, **3** and **4**, respectively, by heating 4,5-diaminophthalonitrile **1** with an excess of acetic, butyric or hexanoic acid.



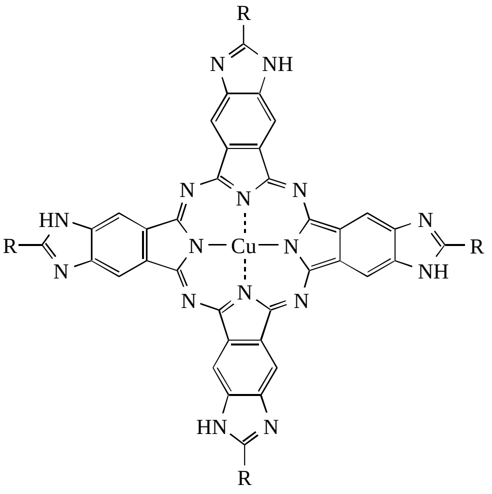
2 R = Me
3 R = Pr
4 R = C_5H_{11}

Compound **4** was also obtained in 40% yield using freshly distilled hexanoyl chloride as a condensing agent. The target products were purified by recrystallisation from water (**2**) or ethanol (**3** and **4**).[†] The use of nonanoic acid or nonanoyl chloride did not produce 2-octyl-5,6-dicyanobenzimidazole. The IR spectrum of a brown tar formed in this case did not exhibit absorption at 1620–1700 cm^{-1} ($\nu_{C=N}$ in the imidazole unit).

The IR spectra[‡] of compounds **2**–**4** contained bands that were assigned to stretching vibrations of the C–H, C–C, N–H, C=N and C≡N bonds; these results are consistent with the published data for other 2-alkylbenzimidazoles.

The band at 1664 cm^{-1}, which was assigned to the C=N bond of an imidazole unit, is of particular importance. The appearance of this band indicates that the condensation reaction proceeded to form dicyanobenzimidazole derivatives.

Compounds **5**–**7** were obtained in 37–67% yields by heating nitriles **2**–**4** with copper acetate (in the 4:1 molar ratio) at 250 °C for 2 h. The reaction products were dissolved in minimum amounts of concentrated H_2SO_4, and water was added to the solutions. The products formed were treated with a 5% NH_3 solution, filtered off and dried at 120 °C. Compounds **5** and **6** were additionally purified by washing with hot methanol. Compound **7** was purified by column chromatography (Al_2O_3, $CHCl_3$: pyridine, 10:1 v/v).



5 R = Me
6 R = Pr
7 R = C_5H_{11}

The electronic absorption spectra (Figure 1) of **5** and **6** exhibit a doublet in the Q-band region with maxima at 715 and 655 nm; this behaviour is not typical of copper phthalocyanine complexes.[7] Furthermore, the Beer–Lambert law was not obeyed at concentrations of 10^{-6}–10^{-5} mol l^{-1}; this fact indicates a tendency to aggregation behaviour in this concentration range. The band at 715 nm can be assigned to the absorption of nonassociated species, whereas the band at 655 nm is due to associated species[8,9] of **5** and **6**. Compound **7** is readily soluble in organic solvents (pyridine, DMF, methanol, acetonitrile, chloroform and benzene). The electronic absorption spectrum of **7** is presented in Figure 1. This spectrum exhibits a broad band in the Q-region at 619 nm, which corresponds to the absorption of completely associated species.

Thus, 2-alkyl-5,6-dicyanobenzimidazoles can be used for the preparation of amphiphilic symmetrical tetrasubstituted phthalocyanines containing four 2-alkylimidazole units. The latter compounds are soluble in nonpolar organic solvents and can be used as materials for the preparation of Langmuir–Blodgett films.

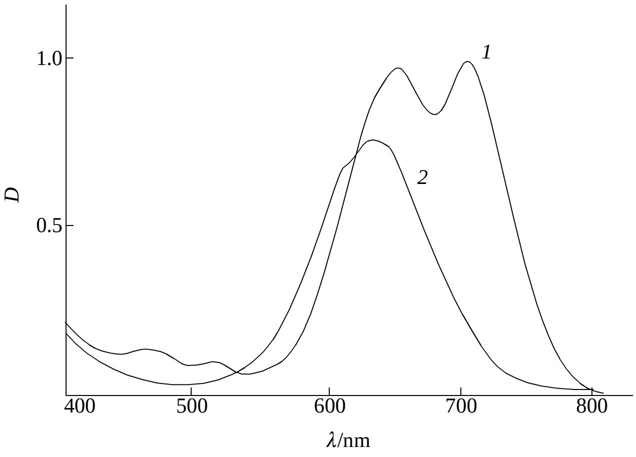


Figure 1 Electronic absorption spectra of (*1*) **6** in DMF and (*2*) **7** in $CHCl_3$.

[†] The purity of **2**–**4** was confirmed by HPLC (a Liquochrom 2010 chromatograph with UV detection).

[‡] IR spectra (in KBr pellets) were recorded on a Specord M-80 instrument. Electronic absorption spectra were recorded on a Specord M-40 instrument. The elemental analysis data for compounds **2**–**7** were in a good agreement with the calculations.

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