A Synthesis of Novel Non-symmetrical Phthalocyanines

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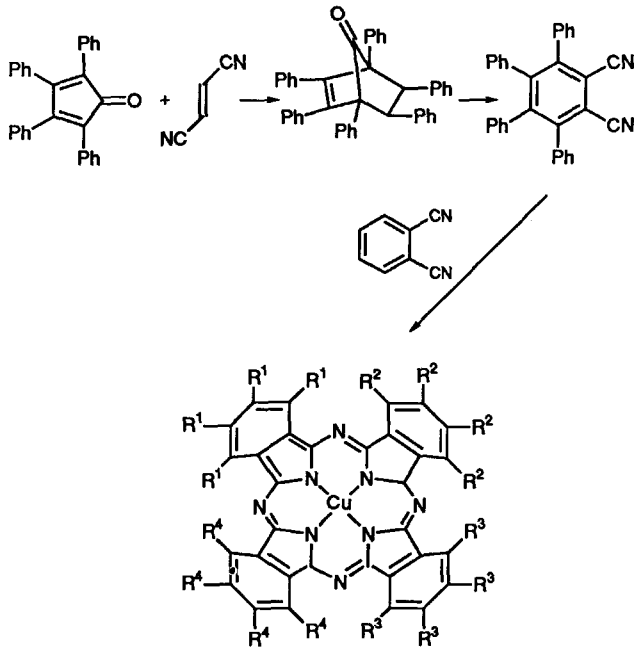
The reaction between tetraphenylphthalonitrile and phthalonitrile in the presence of copper(I) chloride gives a non-statistical mixture of phthalocyanines from which the tetraphenyl-substituted compound **3** can be isolated.

A large number of papers deal with the chemistry, spectral characteristics and use of compounds with a phthalocyanine system.[1,2] In recent years there has been an increasing interest in the chemistry of asymmetrical phthalocyanines[3–5] and porphyrins related to them. These substances are, on the one hand, of interest in terms of studying their chemical and spectral properties, *e.g.* studying the effect of asymmetry in molecules. On the other hand, this is associated with the possibility of using such systems in practice, *e.g.* in Langmuir–Blodgett films.[5] However, there is no suitable method for synthesizing non-symmetrical phthalocyanines as yet.

We have attempted in our study to obtain a non-statistical mixture of non-symmetrical phthalocyanines on interacting two different *ortho*-dinitriles, one of which provided steric hindrance in a template synthesis of a macrocycle. We used tetraphenylphthalonitrile as such an *ortho*-dinitrile, in which *ortho*-phenyl groups provide steric hindrance when *ortho*-dinitriles tetramerize (Scheme 1). The synthesis of the whole series of molecules was carried out at 280–300 °C under argon. A mixture of equimolar amounts of tetraphenylphthalonitrile[6] and phthalonitrile with a two-fold excess of copper(I) chloride was melted in a Wood metal-bath container for 7 h. The cooled melt was treated with water, 5% aqueous HCl, 5% aqueous NH_4OH and water and was then dried. A mixture of non-symmetrical phthalocyanines was dissolved in benzene, boiled down to the minimum volume, and the substances were chromatographed on silica gel using a pyridine–benzene (2:7) mixture.



1 $R^1 = R^2 = R^3 = Ph$; $R^4 = H$ (3:1) isomer
2 $R^1 = R^2 = Ph$; $R^3 = R^4 = H$ (2:2) *cis*-isomer
$R^1 = R^3 = Ph$; $R^2 = R^4 = H$ (2:2) *trans*-isomer
3 $R^1 = Ph$; $R^2 = R^3 = R^4 = H$ (1:3) isomer
4 $R^1 = R^2 = R^3 = R^4 = H$
5 $R^1 = R^2 = R^3 = R^4 = Ph$

Scheme 1

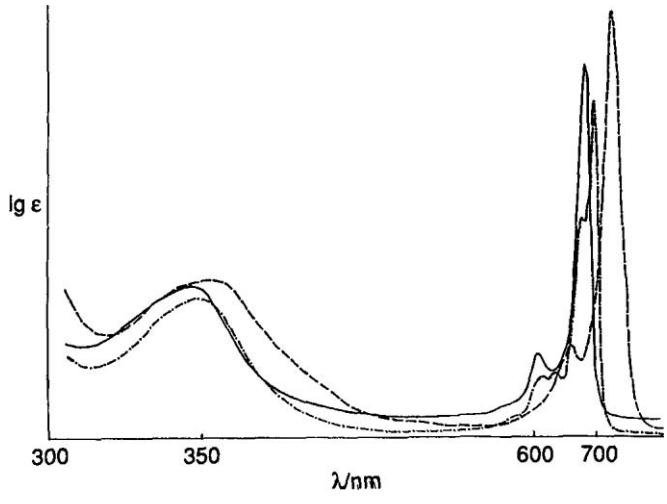


Fig. 1. The electronic absorption spectra of non-symmetrical phthalocyanines **1–3**. Compound **1** (– –), formula $C_{104}H_{64}N_8Cu$, λ_{max}/nm (lg ε): 354 (4.72), 657 (4.65), 730 (5.01). Compound **2** (–.–), mixture of *cis* and *trans* isomers, formula $C_{80}H_{48}N_8Cu$, λ_{max}/nm (lg ε): 350 (4.70), 611 (4.61), 630 (4.62), 675 (4.79), 694 (4.91). Compound **3** (—), formula $C_{56}H_{32}N_8Cu$, λ_{max}/nm (lg ε): 348 (4.71), 609 (4.64), 677 (4.95).

The isolated yield of phthalocyanines from the reaction decreased in the order **4**>**3**>**2**>**1** (24, 20, 14 and 8%, respectively). Symmetrical complex **5** was not detected in the reaction mixture. These facts are in good agreement with the assumption that the template synthesis of a particular compound becomes more difficult with increasing number of phenyl groups in the macrocycle and hence with increasing steric hindrance in the non-symmetrical phthalocyanine molecule. Thus, further addition of an A or B fragment to the A–B dimer (where A is a unsubstituted fragment and B is a substituted one) gives four products: A–B–A (*a*), A–A–B (*b*), B–A–B (*c*) and A–B–B (*d*). In so doing, stress already exists between the B–B fragments in trimer (*d*), and on adding a B fragment to trimers (*b*) and (*c*) followed by their cyclization, this also leads to stress in the macrocycle because of steric hindrance provided by the *ortho*-phenyl goups in the B–B fragments: B–A–A–B and B–A–B–B. Similar considerations are applicable to A–A and B–B dimers. This possibly is the main reason for the observed yields of non-symmetrical compounds **1–3**.

The synthesized compounds are green crystalline substances which are readily soluble in many organic solvents (benzene, chloroform, DMSO, *etc.*).

The mass spectra of compounds **1–3** obtained by fast atom bombardment and secondary ion mass spectroscopy exhibit parent mass peaks 1487 (gross formula:

$C_{104}H_{68}N_8Cu$), 1183 (gross formula: $C_{80}H_{52}N_8Cu$) and 879 (gross formula: $C_{56}H_{36}N_8Cu$), respectively. The elementary analyses agree with the proposed structure ($C_{104}H_{64}N_8Cu$: Found, C 82.64; H 4.36; N 6.94%. Calc. C 83.85; H 4.33; N 7.55%. $C_{80}H_{48}N_8Cu$: Found, C 81.15; H 4.02; N 9.15%. Calc. C 81.06; H 4.08; N 9.49%. $C_{56}H_{32}N_8Cu$: Found, C 76.24; H 3.72; N 12.64%. Calc. C 76.35; H 3.66; N 12.77%). The electronic absorption spectra of synthesized compounds **1–3** were measured in the range 300–900 nm. There is a bathochromic shift of both long wavelength absorption bands and the Soret band in passing from isomer **3** to isomer **1**, *i.e.* with increasing number of phenyl substituents (Fig. 1). Such a shift may be due to some planarity perturbation of the planar molecule because of phenyl group repulsion.

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