

Planar Bisphthalocyanine: a Reinvestigation

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The synthesis and characterization of a new planar bisphthalocyanine derivative substituted with 12-ethylhexyloxy side chains **2b** is described; a similar compound was reported previously, but it is shown here that it probably corresponds to a protonated form of the actual derivative.

The synthesis of planar bisphthalocyanines was claimed to have been achieved a few years ago.¹ Subsequently, the derivative substituted with 12 2-ethylhexyloxy side chains **2a** was shown to form a mesophase.² Surprisingly, no redshift in the optical absorption spectrum was observed when compar-

ing the conventional phthalocyanine **1** and the dimeric derivative **2a**. A new compound **2b** (Fig. 1) has been isolated and characterized which does demonstrate the expected redshift.

By reacting 4,5-bis(2-ethylhexyloxy)-1,2-phthalonitrile with

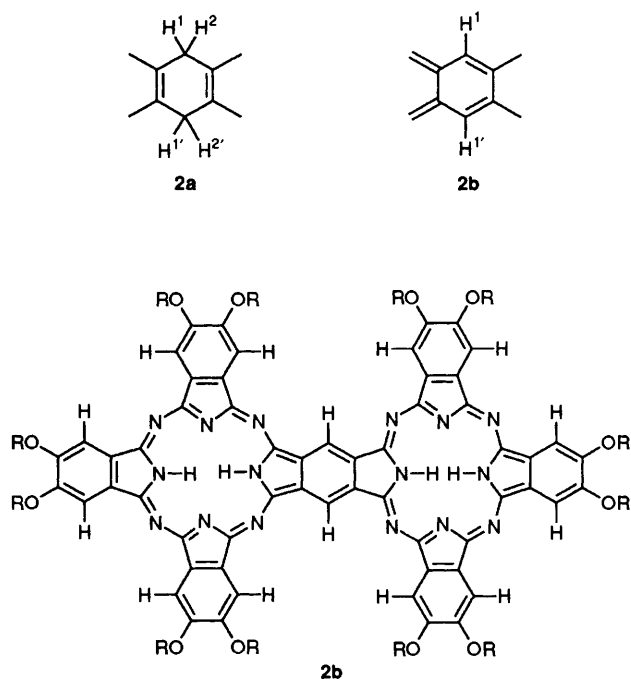


Fig. 1 Planar bisphthalocyanine **2b** synthesized in the present study

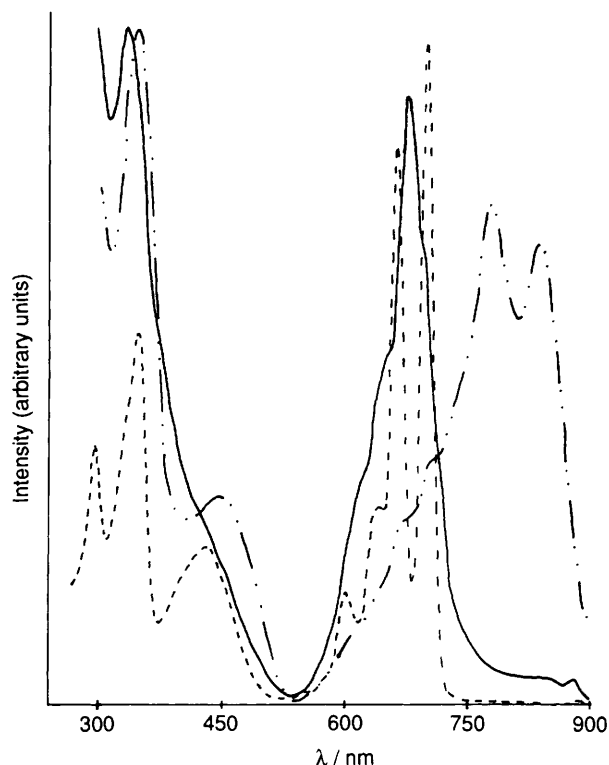


Fig. 2 Optical absorption spectra of **1** (---), **2a** (—) and **2b** (— · —) in CH_2Cl_2 (the spectra are insensitive to concentration changes)

bisdiiminoisindole,¹ at least three products are obtained: **2a** and the metal free phthalocyanine **1** mixed with a species **2b** in the chromatography fractions (SiO_2 ; eluent: toluene). A further purification is carried out by dissolution of **1** in ethyl acetate in which **2b** is insoluble, followed by preparative TLC (SiO_2 ; eluent: toluene) (overall yield: 5%). Compound **2b** shows a significant redshift in its absorption spectrum when compared to **1** and **2a** (Fig. 2).

Field desorption mass spectrometry permitted us to unambiguously characterize **2b**. The parent ion ($M^+ = 2486$) and aggregated species ($2M^+$, $3M^+/2$ and $3M^+/2 - 484$), have been observed. The same behaviour is found for unsubstituted phthalocyanines.³ In the case of **2a**, the parent ion was not detected. The fragmentation pattern is identical for the two compounds. ^1H NMR, ^{13}C NMR and elemental microanalysis of **2b** are in agreement with the proposed structure.† All determinations seem to indicate that **2a** and **2b** differ by the presence of two extra hydrogens on the six-membered ring linking the phthalocyanine subunits. The ^1H NMR in the region 8–10 ppm shows, as expected only one broad peak at δ 10.5 for **2b** corresponding to H^1 and $\text{H}^{1'}$, whereas **2a** lead to a more complicated pattern.²

A few structurally related compounds were described in the literature with crown ether linked binuclear phthalocyanines,⁴ linearly conjugated tetrakisporphyrins⁵ and a binuclear tetrabenzoporphyrin derivative,⁶ but this is the first time that the compound **2b** is described and thoroughly characterized.

An anisotropic phase is observed for **2b** by polarized light microscopy from room temp. to 300 °C. No transition is detected by differential scanning calorimetry. However, small-angle X-ray diffraction indicates an orthorhombic lattice ($a = 42$, $b = 28$ Å) at room temp. and 200 °C and a square symmetry ($a = b = 25$ Å) at 300 °C. Compound **2a** demonstrated a lamellar mesophase ($c = 21.6$ Å).² The monomeric substituted phthalocyanine **1** showed a tetragonal mesophase ($a = 23.3$ Å) and a nematic liquid crystalline phase.⁷

The copper derivative **2b**, **Cu** has also been synthesized and fully characterized.

In conclusion, planar bisphthalocyanine derivatives have been obtained for the first time. Previous studies¹ erroneously assigned the same structure to other compounds. A conjugation of the π -electrons between the two sub-macrocycles is evidenced by optical absorption spectra. The magnitude of the copper–copper coupling will be determined by EPR for the metallic complex **2b**, **Cu**.

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† **2b** Microanalysis: $\text{C}_{154}\text{H}_{222}\text{N}_{16}\text{O}_{12}$ ($M^+ : 2489.55$): Calc.: C: 74.30; H 8.99; N: 9.00. Found: C: 73.68; H: 8.87; N: 8.91%. ^1H NMR (CS_2 : in all other solvents, aggregation occurs) δ -2.9 (4H, NH), 1–2.2 (180 H, CH, CH_2 , CH_3), 4.5 (24 H, OCH_2), 8.4–8.6 (12 H, arom.), 10.5 (2 H, arom.). ^{13}C NMR (CS_2) δ 12.6, 15.1 (CH_3), 24.3, 25.0, 30.4, 31.6, 31.9 (CH_2), 40.8, 41.0, (CH), 72.1, 72.9 (OCH_2), 104.7, 106.7 (CH arom.), 116.9 (CH arom.), 127.7, 133.9, 139.0, 142.7, 152.5, 153.2, 155.6, 156.7 (arom.).