Low Symmetrical Phthalocyanines Having Spectroscopic and Electrochemical Properties Characteristic of Unexpected Accidental S_1 State Degeneracy and Non-Planar Distortions

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Low-symmetrical phthalocyanines (Pcs) **2**-**5** prepared by mixed condensation of tetraphenylphthalonitrile and 4-phenylthiophthalonitrile in the presence of a copper salt, show spectroscopic, electrochemical, and molecular model indications which suggest varying degrees of non-planar distortions of the Pc plane and unexpected S_1 state degeneracy.

In contrast to porphyrins, phthalocyanines (Pcs) are very planar[1] and accordingly show properties ascribable to this planarity, such as one-dimentional stacking. From the studies on porphyrins,[2] it has been conjectured that introduction of a number of bulky substituents onto the Pc periphery could increase the non-planar distortion of the Pc plane. However, no one has yet succeeded in presenting evidence of this kind of distortion in Pcs which should variy according to the number of introduced substituent groups. In this communication, we report a series of low symmetrical Pcs which show varying degrees of spectroscopic and electrochemical properties characteristic of non-planar distortion, and surprisingly, even accidental S_1 state degeneracy.

Using the concept of sterically directed synthesis for low symmetrical Pcs,[3] 4-phenylthiophthalonitrile (α unit) and tetraphenylphthalonitrile (β unit) were reacted in the presence of $CuCl_2$ at 260 °C for 40 min, and the products were separated by column chromatography, to give Pcs **1**; αααα, **2**; αααβ, **3**; αβαβ, **4**; ααββ, and **5**; αβββ types.[4] Despite steric hindrances due to the phenyl groups at the 3 and 6 positions of tetraphenyl-phthalonitrile, Pcs **4** and **5** were obtained in moderate yields, plausibly because of a use of a strong template (copper ion) and high temperature.[3cd,5] In order to obtain NMR data for these ring systems, attempts were made to incorporate a diamagnetic metal instead of copper. However, when zinc or magnesium ions were used in the synthesis, no sterically hindered unsymmetrical Pcs were obtained, in agreement with a recent report.[3a] Pcs **1**, **2** and **5** were easily identified from the mass data; however the discrimination between Pcs **3** (opposite type) and **4** (adjacent type) which gave the same parent ion peak in the mass spectra (m/z = 1401, $[M+H]^+$) was performed on the basis of the knowledge of the position, intensity, and shape of the Q_{00} band. Namely, since it is known that a non-planar, distorted porphyrin shows a broader Q_{00} band with a lower absorption coefficient and a shift to a longer wavelength,[2] Pc **4**, which appears to have higher distortion due to steric hindrance between two phenyl groups belonging to adja-

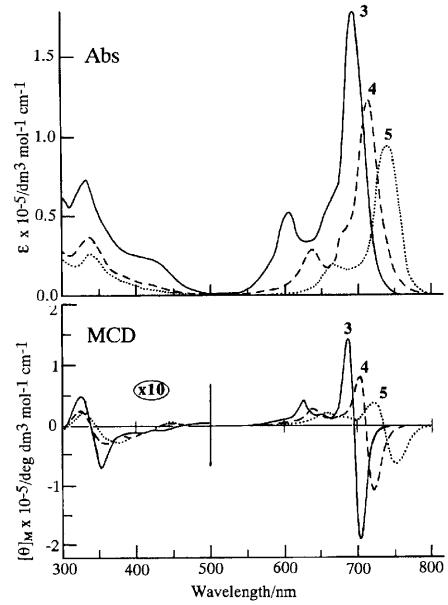

Figure 1. Electronic absorption (top) and MCD spectra (bottom) of compounds **1**, **2**, and **3** in chloroform.

Table 1. Electronic absorption, cyclic voltammetric, and deviation from planarity data for Pcs **1**-**5**

Pc	$E_{1/2}$/V (SCE)[a]				Absorption				Deviation from
	E_{ox2}	E_{ox1}	E_{red1}	E_{red2}	λ/nm (log ε)[b]				planarity[d]
1	1.19[c]	0.73	-0.98	-1.26	694(5.24),	627(4.61),	414(4.33),	343(4.91)	0°
2	1.22[c]	0.79	-0.92	-1.23	696(5.20),	627(4.56),	414(sh),	347(4.82)	0°
3	1.24[c]	0.82	-0.90	-1.16	696(5.23),	631(4.74),	414(sh),	347(5.04)	0°
4	1.09[c]	0.64	-0.99	-1.27	715(5.08),	642(4.40),	414(sh),	343(4.61)	20.1°
5	1.05[c]	0.60	-1.07	-1.37	741(4.98),	666(4.33),		348(4.53)	28.9°

[a] Cyclic voltammetric data were collected in DCB containing TBAP (0.1 M). All potentials were corrected to Fc/Fc^+ couple. [b] In chloroform. sh means shoulder. [c] Irreversible peaks. Half-wave potentials were estimated by $E_{1/2}$ = ($E_{anodic\ peak}$ + $E_{cathodic\ peak}$)/2. [d] Degree of non-planarity has been estimated as a sum of isoindole fragments' deviations from the central N_4 plane of the Pc macrocycle.

cent benzene rings of Pcs, is assigned as the Pc which shows the longer-wavelength Q_{00} band to longer wavelengths. This assignment is further supported by comparison with the data on low symmetrical NiPcs prepared by mixed condensation of tetraphenylphthalonitrile and phthalonitrile.[5] In addition, cyclic voltammetric data as well as molecular modeling data also support our assignments (see below).

Figure 1 shows the electronic absorption and MCD spectra of Pcs **3**-**5**, and Table 1 summarizes the main absorption, redox and some molecular modeling data of all the Pcs.[6] As can be seen from the results, there is no splitting of the Q_{00} band, suggesting that the two LUMOs in these compounds are accidentally nearly degenerate, despite their low symmetry. This near degeneracy is also supported by the presence of Faraday *A* terms associated with the Q_{00} bands. Since most D_{2h} type Pcs so far reported have relatively large splitting energy,[7] which is theoretically supported,[8] the fact that even Pc **3**, having D_{2h} symmetry, does not show a clear splitting deserves attention. S_1 state degeneracy is expected only when the effective chromophore symmetry is D_{4h}.[9] Accordingly, the unsplit Q band in low symmetrical Pcs **2**-**5** indicates that the sum of the perturbation power of one phenylthio- and three hydro groups in the phenylthioisoindolediimine fragment of the Pc π-system is approximately equal to that of four phenyl groups in the tetraphenylisoindolediimine fragment. Close inspection of the data in Table 1 lends support to this conclusion, since the differences between the first oxidation and reduction potentials and the positions of both the Soret and Q bands in Pcs **1**-**3** resemble to one another, even thougth they consist of different numbers of phenylthioisoindolediimine and tetraphenylisoindolediimine units. Data for Pcs **4** and **5** *per se* can be rationalized as arising from the increase in the extent of non-planarity.[2] The shift of the Q band to longer wavelengths with accompanying reduction of intensity on going from Pcs **3** to **4** and further to **5** is in accord with the increase in steric hindrance between adjacent tetraphenylisoindole units (viz. non-planarity, as can be deduced from the molecular modeling data in Table 1). This in turn is associated with the smaller energy differences between the first oxidation and reduction potentials in **4** and **5** (average 1.65 V) compared to **3** (1.72 V). In particular, the cathodic shift of the first oxidation and reduction potentials in Pcs **4** and **5** compared with those of **3** suggests that the longer wavelength shift of the Q band is related to the destabilization of both HOMOs and LUMOs, although the extent is larger for the HOMOs, judging from the values of the redox potentials. These observations on Pcs **3**-**5** constitute the first example of a quantitative explanation of the influence of non-planar distortions on the spectroscopic and electrochemical behavior of low symmetrical Pcs. It is noteworthy that the opposite type Pc **3** does not show any splitting in the Q band and that even the most non-planar Pc **5** shows spectra which suggest degeneracy in the first excited states. This kind of Pc has not been reported to date.

In conclusion, we have shown a series of low symmetrical Pcs which have varying degrees of distortion of the Pc plane. In particular, it is notable that even D_{2h} type Pcs and most distorted Pcs showed spectra which suggest unexpected accidental S_1 state degeneracy.

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6 An optimized structure of Pc **5**, electronic and MCD spectra of complexes **1** and **2**, and high resolution FAB mass patterns of Pcs **1**-**5** are obtainable on request.

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