

Extremely Non-Planar Phthalocyanines with Saddle or Helical Conformation: Synthesis and Structural Characterizations

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Most of the applications of phthalocyanines (Pcs) are concerned with the large, flat π -conjugation system, as well as the type of central metal.¹ In particular, it is well-known that, compared with porphyrins,² the metalloPcs (MtPcs) have extremely high planarity: for example, nonsubstituted NiPc is essentially perfectly planar,³ although MtPcs with larger metal ions such as Pb and Sn distort the geometry to some extent.⁴ Structurally distorted Pcs have been reported in the past few years, where the steric congestion of substituents caused distortion of the macrocycle.^{4,5} In this communication, we report two types of Pc analogues whose nonplanarity appears to be the highest yet reported. To induce the largest distortion conceivable, aromatic ortho-dinitriles having two protruding phenyl groups, **3** and **4**, are used. These types of dinitriles have long been believed to be too congested to form Pcs by themselves⁶ and have therefore been employed for the preparation of *opposite* type of MtPc analogues, utilizing the steric hindrance between the phenyl groups.⁷ In the course of studies, however, we thought that, if these dinitriles can occupy the *adjacent* positions of Pcs, the deviation from planarity would be very large because of the overlap of the protruding phenyl groups.⁸ As described below, we have overcome this problem, and the resultant two Pc analogues obtained by the above inverse concept, **1** and **2**, are indeed confirmed to be the most nonplanar Pcs ever substantiated structurally.

Both **1**⁹ and **2**¹⁰ were prepared by the so-called lithium method¹ at ca. 170 and 150 °C, respectively (Scheme 1). In the case of **2**, dinitriles **4** and **5** were co-macrocyzled, so that repeated

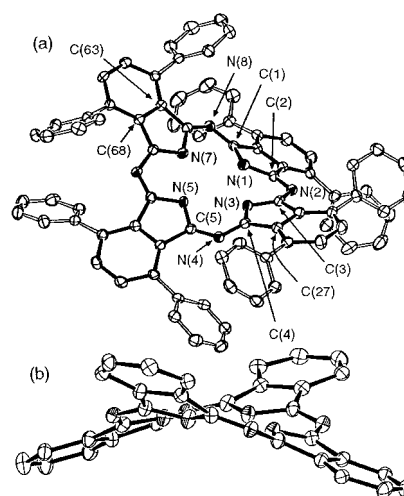
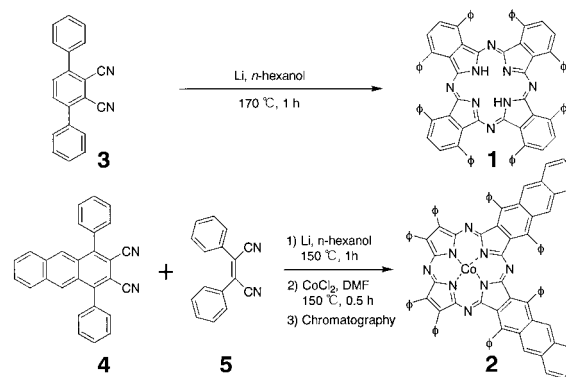


Figure 1. View of the molecular structure of **1**: (a) top view and (b) side view. Displacement ellipsoids are shown at the 50% probability level. Hydrogen (in both (a) and (b)) and phenyl groups (in (b)) are omitted for clarity.

Scheme 1



(1) (a) *Phthalocyanines-Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, Germany, 1989, 1993, 1993, and 1996; Vols. I–IV. (b) Shirai, H., Kobayashi, N., Eds.; *Phthalocyanines-Chemistry and Functions*; IPC: Tokyo, 1997.

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(9) Synthetic procedure and some spectroscopic data for **1**: Lithium (100 mg, 15 mmol) was heated at 100 °C in 1-hexanol (5 mL) until all of the metal was dissolved. After cooling to room temperature, diphenylmalonitrile (1 g, 3.6 mmol) was added and reacted for 1 h at 170 °C. Most of the solvent was boiled off, DMF (5 mL) was added, and the mixture was poured into 200 mL of water. The precipitated solid was filtered off, washed with water and methanol, and dried under reduced pressure. The crude products were further purified using column chromatography (silica, toluene–cyclohexane (1:1 v/v)) to give 40 mg (4.0%) of **1** ($R_f = 0.7$) as a yellowish green solid. FAB mass (m/z): 1123 ($M^+ + 1$). Anal. Calcd for $C_{80}H_{50}N_8$: C, 85.54; H, 4.49; N, 9.98. Found: C, 85.50; H, 4.74; N, 9.80. 1H NMR (toluene- d_6 , 400 MHz at 0 °C): δ 7.47 (s, 8H, Pc), 7.45 (d, 16H, phenyl *o*-H), 7.18 (t, 8H, phenyl *p*-H), 7.10 (dd, 16H, phenyl *m*-H), 2.02 (–60 °C) to 2.12 (100 °C) (s, 2H, NH) (at 0 °C, NH signal is not detectable hidden by CH_3 signal of the solvent). UV–vis (CHCl₃, λ , nm (lg ϵ): 788 (4.96), 699sh (4.37), 414sh (4.39), 336 (4.58), and 281sh (4.91).

chromatography was inevitably required. They were characterized using mass spectra, elemental analysis, and 1H NMR (only for **1**)^{9,10} and their molecular structures were analyzed by X-ray crystallography. Crystals were grown in either chloroform–hexane (**1**) or acetone-containing toluene (**2**).

Figures 1 and 2 show ORTEP drawings of **1**¹¹ and **2**,¹² respectively. As expected, the steric hindrance arising from the substituted phenyl groups appears quite significant in deforming the Pc skeleton. For **1**, the most significant structural characteristic is an alternating up-and-down displacement of the individual isoindole units from the mean plane generated by the four pyrrole nitrogens (4N-plane). This type of structure has been termed a saddle conformation.² Figure 3 (top) shows the skeletal deviation

(10) Synthetic procedure and some spectroscopic data for **2**: Lithium (100 mg, 15 mmol) was heated at 100 °C in 1-hexanol (5 mL) until all of the metal was dissolved. After cooling to room temperature, diphenylmalonitrile (180 mg, 0.78 mmol) and 2,3-dicyano-1,4-diphenylanthracene (250 mg, 0.66 mmol) were added and reacted for 1 h at 150 °C. Most of the solvent was boiled off, DMF (30 mL) and $CoCl_2$ (1.4 g, 11 mmol) were added and maintained at 150 °C for 30 min. The mixture was poured into 200 mL of water, and the resultant solid filtered off, washed with water and methanol, and dried. The residue was purified using preparative TLC (silica, toluene), to give 40 mg (9.5% on the basis of the dicyano-diphenylanthracene) of **2** ($R_f = 0.83$) as a green solid. FAB mass (m/z): 1280 ($M^+ + 1$). Anal. Found: C, 81.98; H, 4.33; N, 8.65. Calcd for $C_{88}H_{52}N_8Co$: C, 82.55; H, 4.09; N, 8.75. UV–vis (toluene, λ , nm (lg ϵ): 748 (5.89), 669sh (5.49), 490 (5.17), 425sh (5.43), and 355 (5.89). Another green band was recognized at $R_f = 0.68$, and this portion was identified as monoanthracene-fused TAP (16 mg, 5.4% based on diphenylmalonitrile).

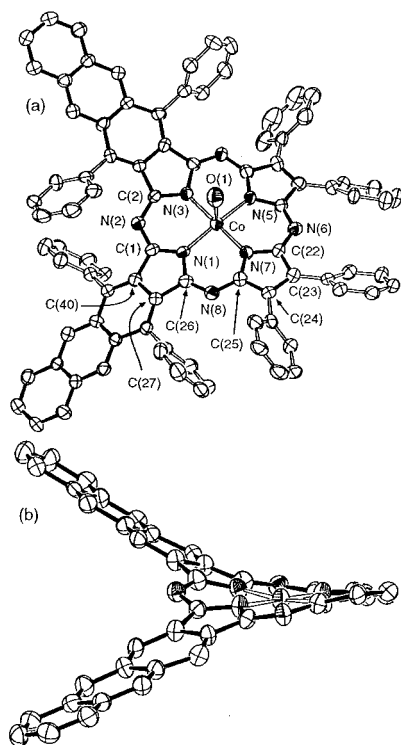


Figure 2. View of the molecular structure of **2**: (a) top view and (b) side view. Displacement ellipsoids are shown at the 50% probability level. Hydrogen (in both (a) and (b)) and phenyl groups (in (b)) are omitted for clarity.

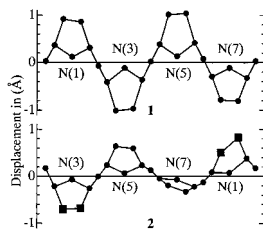


Figure 3. Linear display of the out-of-4N-plane deviations from planarity for the core atoms of **1** (top) and **2** (bottom). Squares indicate the carbon atoms fused to anthracene rings.

of the central 20-membered macrocyclic atoms of **1** from the 4N-plane. The observed maximum deviation is ca. 1.03 Å, which is the largest observed thus far for Pcs, and even compares with those of the representative highly disordered porphyrins (ca. 0.7–1.4 Å),² even though Pcs, unlike porphyrins, cannot have bulky substituents structurally at their meso-positions which are important in deforming the π -conjugation plane. The degree of deviation of the other pyrrole units is approximately in the same order (ca. 1 Å). The dihedral angles between the pair of planes formed by

(11) Crystallographic data for **1**: single crystals of **1** containing CHCl_3 and hexane were obtained by recrystallization from a CHCl_3 /hexane solution. $\text{C}_{82.51}\text{H}_{55.11}\text{N}_8\text{Cl}_{1.68}$, triclinic, space group $P-1$ (No. 2), with unit-cell dimensions $a = 15.5258(5)$ Å, $b = 15.8918(7)$ Å, $c = 16.4589(2)$ Å, $\alpha = 87.287(2)^\circ$, $\beta = 67.873(2)^\circ$, $\gamma = 61.084(3)^\circ$, $V = 3247.1(2)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.246$ g/cm³. Intensity data were collected at 150 K on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods and expanded using Fourier techniques; 25149 reflections were measured in which 13169 were independent. Final $R_1 = 0.094$, $R_w = 0.219$ ($I > 2.0 \sigma(I)$). Full details are described in the Supporting Information.

(12) Crystallographic data for **2**: $\text{C}_{105}\text{H}_{92}\text{N}_8\text{CoO}_6$, monoclinic, space group $C2/c$ (No. 15), with unit-cell dimensions $a = 31.460(9)$ Å, $b = 20.602(4)$ Å, $c = 28.041(3)$ Å, $\beta = 115.608(1)^\circ$, $V = 16389(5)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.314$ g/cm³. Intensity data were collected at 150 K on a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods and expanded using Fourier techniques. A total of 49418 reflections were measured in which 16857 were independent. Final $R_1 = 0.086$, $R_w = 0.097$ ($I > 2.0 \sigma(I)$). Full details are described in the Supporting Information.

the isoindole units on either side of the core reach 46.0 and 41.9° (43.9° on average), which are well above the recently reported value for 1,4,8,11,15,18,22,25-octaisopentyl Pc by Cook et al. (32.0°)⁵ and is unambiguously the largest deformation seen in the Pc derivatives known to date. As seen in Figure 1, the deformation seems to originate mainly from twisting around the meso-N atoms, that is each isoindole unit retains a relatively high planarity (see Supporting Information) and the twisting among isoindole units dominates the total molecular structure. On the other hand, despite being a nonplanar macrocycle, the bond lengths in **1** are close to those found in nonsubstituted planar H_2Pc .¹³ For example, bond lengths of N1–C1, N8–C1, C4–C27, and C63–C68 are 1.372(4), 1.331(4), 1.480(5), and 1.419(4) Å, respectively, while the corresponding bond lengths in H_2Pc are 1.34, 1.33, 1.49, and 1.39 Å, respectively.¹³

The ORTEP drawing in Figure 2 clearly illustrates that compound **2**¹² is a tetraazaporphyrin (TAP) adjacently fused by two anthracene rings. Similarly to **1**, **2** is conformationally highly stressed due to the peripherally substituted phenyl groups, and therefore the whole molecule adopts a kind of helical structure. In other words, the structure of **2** is similar to helicene, although no significant vertical overlap between π orbitals is conceivable. As far as we know, this is the first realization of a helical structure using low symmetrical Pcs or porphyrins. The dihedral angle between the neighboring planes formed by the two adjacent isoindole units (i.e., outer naphthalene rings have been ignored to compare the two compounds) is 40.5°. On the other hand, the values in **1** are 29.6, 30.1, 31.3, and 32.0° (30.7° on average), which is, interestingly, much smaller than those in **2**. It is intuitively anticipated that central metals whose sizes fit into the Pc cavity (such as cobalt, nickel, etc.) reduce the skeletal deformation. Accordingly, these experimental results, which are wholly contrary to our expectations, might be considered to result from the low symmetrical π -conjugation system of **2**. Since the two anthracene units are such large substituents on the TAP skeleton, the interaction of these two units primarily determines the whole molecular structure, dominating the ring-planarizing effect of the metal. Figure 3 (bottom) shows that the skeletal deformation is particularly marked for the pyrroles fused to anthracene rings (ca. 0.5–0.8 Å) and the deviations of the other pyrroles are somewhat smaller (ca. 0.2–0.6 Å), emphasizing the helical structure of **2** (Figure 2b).

In summary, we have prepared two novel, structurally highly deformed Pc derivatives and determined that they adopt either saddle or helical conformations depending on the geometry of the π -conjugation system. They have been identified to have the most deformed macrocyclic core in the Pcs and TAPs thus far determined in the solid state. In particular, **2** is the first helicene-like compound found in the porphyrin and Pc family. Compared with normal flat Pcs and TAPs without substituents, the bond lengths are virtually unchanged. Hence, the structural deformation appears to originate primarily from strain of the bond angles. Although we used 3,6-diphenylphthalonitrile and zinc ion to obtain oppositely substituted Pcs in our previous papers,^{7a,b} the use of a stonger template, that is lithium ion, made it possible to prepare sterically crowded **1** and **2**. Detailed spectroscopic and electrochemical properties of **1**, **2** will be reported in due course.

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Supporting Information Available: X-ray data for **1** and **2** (CIF and PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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