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Note

1,15-Bis-(2′,2′,4′-trimethyl-3′-pentoxy)phthalocyanine, a *trans*-form nonperipheral di-substituted phthalocyanine synthesized by the ‘cross condensation’ method

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Abstract

The crystal structure of **1**, 15-bis-(2′,2′,4′-trimethyl-3′-pentoxy)phthalocyanine was determined what confirmed the ‘cross condensation’ method for the ABAB type phthalocyanine and the *trans*-form arrangement of the two substituents suggested that the alkoxy group also affected the condensation mechanism.

Keywords: Phthalocyanine; Crystal structure; Cross condensation

Phthalocyanines (Pcs) have been studied widely for their uses as functional dyes. Recently we have synthesized a series of ring substituted Pcs and studied the effects of substituents on their aggregation behaviors, skeletal conformations, and stabilities in oxidation environment by crystal structural and spectral methods [1–3]. As a non-uniformly substituted ABAB type Pc, the title compound **1** was synthesized by the ‘cross condensation’ method invented by Young [4]. The single crystal of **1** suitable for X-ray diffraction analysis was obtained from the solution of **1** in pyridine unexpectedly [5], though we were worried about that the condensation product would be a mixture of *trans*-form and *cis*-form for the substituents distribution. The crystal structure determined not only confirmed the method of ‘cross condensation’, but also suggests that the alkoxy substituents at the ortho-position of the phthalonitrile have some effects to the mechanism of condensation.

As shown in Scheme 1 [6], 1,3,3-trichloroiso-indoline (**2**) was condensed together with 4-(2′,2′,4′-trimethyl-3′-pentoxy)-1,3-diiminoisoindoline (**3**) which was prepared from the corresponding alkoxy substituted phthalonitrile, to obtain the title compound **1**. As reported by Young [7], Nickel chloride was added to increase the yield of the product, where no nickel phthalocyanine was found according to the UV–Vis and mass spectra measurements. But from the crystal diffraction data of compound **1**, there was an electron density peak at the centre of the molecule which was feasible to treating as small amount of nickel phthalocyanine, about 5.6% according to the site occupation factors. Therefore, the trace nickel phthalocyanine was produced in the condensation as well but not found in the UV–Vis because of the band overlap and in the mass spectra as a small noise like peak.

The molecular structure of the title compound **1** is shown in Fig. 1. Analogous to the uniformly tetra-substituted phthalocyanine **4** with same substituents [8], the two branches of the substituents may be statistically distributed up and down the ring plane, the five methyl groups of some substituents were represented by six methyl groups in this structure with the sum of their occupation factors to be restrained at five, and the others were not treated to show their disorders. Simultaneity, its molecular structure

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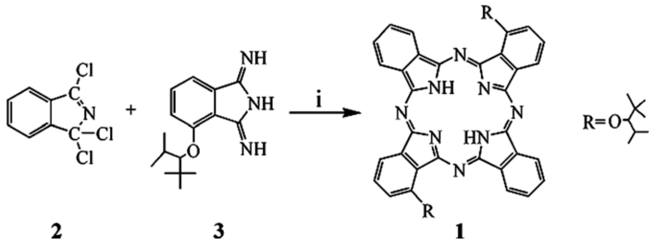

Scheme 1. Reagents and conditions: (i) THF, triethylamine, 0 °C for 1 h and RT for 5 h, then adding $NiCl_2$ for 12 h, followed by adding hydroquinone and CH_3ONa, 85 °C for 8 h.

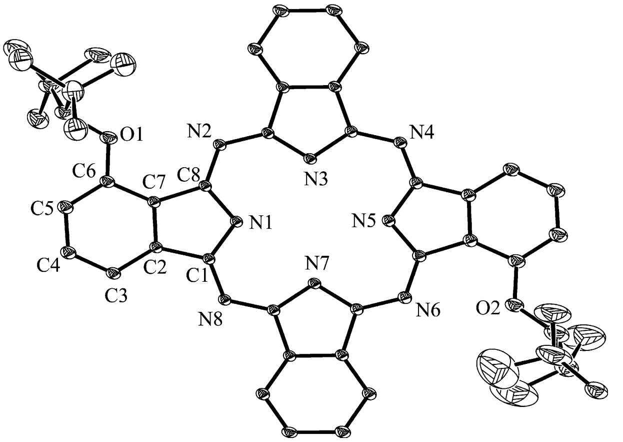

Fig. 1. Molecular structure of compound **1**. Small amount of nickel atom at the centre of inner ring was not presented to dispel possible misunderstanding as a centre metal atom.

reveals clearly that the distribution of the two alkoxy groups are arranged in a *trans*-form. This *trans*-form distribution could be understood from their steric barrier effect in the condensation. Meanwhile, the electronic effect of the alkoxy group cannot be ruled out, which may also affect the reaction activity of the two imino groups in the condensation.

Fig. 2a shows the packing of **1** in crystal. There are two independent molecules aggregated together to form a molecular pair in a unit cell, with a distance of 3.366 Å which is just the thickness of normal aromatic system. And the pairs are separated by the bulky alkoxy groups arranged at the four corners of the pair, as shown in Fig. 2b. But, compared with compound **4**, it is found that the ring skeleton of compound **1** deviates from the planar conformation (Fig. 2c) for its substituents decreased. In addition, the distortions are different for the two molecules in the pair. One of them is a dome shape with angles of 4.784° and 18.247° between the opposite isoindole units, and the other is a saddle one with angles of 6.040° and 6.328°. The different conformations of the two Pc rings are perhaps attributed to different environment [9].

The UV/vis absorption spectra of compound **1** showed a typical split Q band of metal-free Pc, as shown in Fig. 3.

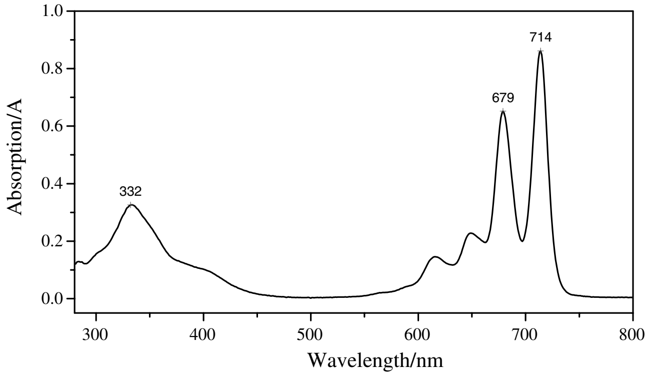

Fig. 3. Electronic absorption spectrum of 1 in toluene.

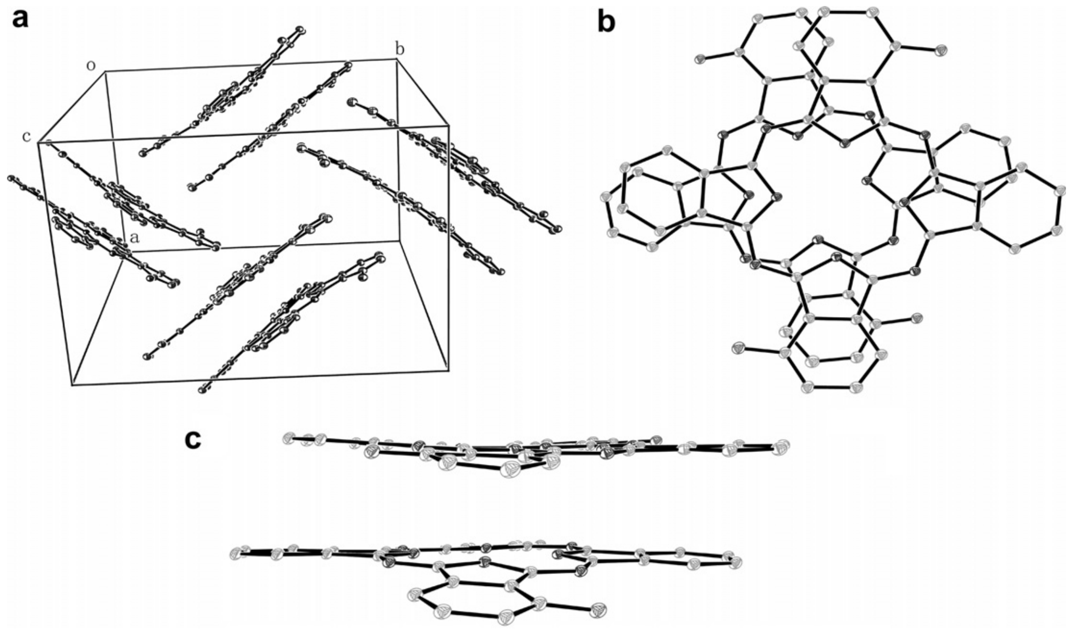

Fig. 2. The packing of 1 in crystal (a), the overlap (b) and side view (c) of molecule pair, where the alky groups were omitted for clarity.

However, the intensity difference of the two peaks is somewhat larger than those of non-substituted or uniformly tetra- and octa-substituted metal free phthalocyanines. This intensity difference can be explained by the electronic effect of the non-uniformly substitution [10].

In conclusion, this structural determination not only confirmed the ‘cross condensation’ method, it also suggested that by use of steric and electronic effect of substituents, simultaneously, some more unique non-uniformly substituted Pcs could be synthesized.

Supplementary

CCDC 602016 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk).

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[5] Crystal data of **1**: $C_{50}H_{48}N_8O_2$, $M = 770.96$ (with about 5.6% of $C_{50}H_{48}N_8NiO_2$, $M = 827.64$), monoclinic, space group $P2_1/a$, $a = 15.520(5)$ Å, $b = 19.063(4)$ Å, $c = 29.528(8)$ Å, $\beta = 101.172(11)°$, $V = 8571(4)$ Å^3, $Z = 8$, $D_c = 1.173$ g cm^{-1}, $F(000) = 3155$, $T = 298(2)$ K, $\mu = 0.078$ cm^{-1}, λ(Mo Kα) = 0.71069 Å, Rigaku *R*-axis imaging plate diffractometer. 75,819 reflections recorded of which 19362 unique ($R_{int} = 0.0928$), 8240 ‘observed’ with $I > 2\sigma(I)$. Structure was resolved by direct method and refined on F^2. Hydrogen atoms were all ‘riding’ at idealized positions, except the disordered alkyl branches where no hydrogen atoms were added. Final $wR_2 = 0.3433$ and $R_1 = 0.1819$ for all 19,362 reflections, $wR_2 = 0.2804$ and $R_1 = 0.0990$ for 8240 reflections with $I > 2\sigma(I)$.

[6] Synthetic procedure of 1,15-bis-(2′,2′,4′-trimethyl-3′-pentoxy)phthalocyanine, 1: A solution of 4-(2′,2′,4′- tirmethyl-3′-pentoxy)diiminoisoindoline (0.90 g, 3.29 mmol), triethylamine (0.96 mL) in dry THF (90 mL) was cooled to 0 °C, then another solution of 1,3,3-trichloroisoindolenine (0.750 g, 3.41 mmol) in dry THF (60 mL) was gradually added under a slow stream of nitrogen. The reaction was carried out with stirring for 1 h at approximately 0 °C then slowly warmed to room temperature over a 5-h period. After the insoluble triethylamine hydrochloride was removed, nickel chloride (0.441 g) was added to the solution and stirred for further 12 h. Then, hydroquinone (0.375 g, 3.40 mmol) and sodium methoxide (0.3 g Na in 5 mL menthol) was added to the reaction vessel and a reflux condenser was equipped. Then the reaction solution was refluxed under nitrogen for 6 h, cooled to room temperature, filtered, and the solvent was stripped from the filtrate leaving a dark blue-black residue. The residue was washing by boiling water and distilling in SOXHLET extractor with menthol and acetone until the filtrate was clear; and then recrystallized times with chloroform. Yield 0.289 g, 22.8%; IR (KBr, cm^{-1}): 1583.1 (C=N), 3274.9 (N–H), 1266.5, 1108.3 (Ar–O–C), 1490.9 (C=C), 2955.6, 2866.4 (CH_3); ^{1}H-NMR ($CDCl_3$)δ: 9.213, 7.993, 7.676 (m, m, m, 14H, H-Pc), 4.759 (m, 2H, –CH –O), 2.608 (m, 2H, –CH–), 1.346–1.318(t, 12H, –C(CH3)2), 1.507–1.496(s, 18H, –C(CH3)3), −1.423 (m, 2H, H–N). MS: *m*/*z* (M+) 772.0, 1542.4 (aggregated molecular pair); UV–vis-near IR (Q band, toluene, nm): 679, 714.

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