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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1063). Services for accessing these data are described at the back of the journal.

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β Metal-free phthalocyanine

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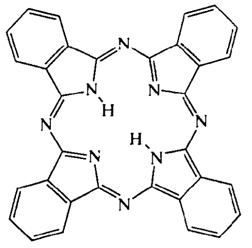
Abstract

The molecule of the title compound, $C_{32}H_{18}N_8$, is slightly distorted at the corners. Two of the phenyl rings are located below the molecular plane while the other two are above the plane. This leads to a molecular symmetry of C_i as opposed to D_{2h}, assumed for the free molecule. The crystal data are basically in good agreement with the β phase reported by Robertson [*J. Chem. Soc.* (1936), pp. 1195–1209], whereas the geometrical parameters are slightly different.

Comment

Metal-free phthalocyanine (MfPc) is a commercial blue pigment which is widely used in the paint and automobile industries. Besides its use as a pigment, MfPc has also attracted attention as a photoconductor for laser printers based on GaAsAl laser diodes (Loutfy *et al.*, 1988). Several crystal modifications such as α, β, *X etc.* are known to exist from X-ray powder diffraction, among which only the β phase has been fully analyzed on the basis of single crystals (Robertson, 1936).



MfPc

In the course of our studies on the mechanism of the near-IR absorption of titanylphthalocyanine (TiOPc), used practically for laser printers, we found that the molecules are heavily deformed upon crystallization ($C_{4v}\rightarrow C_1$) (Mizuguchi *et al.*, 1995). It was also pointed out that the molecular distortion (reduction in symmetry) has a profound influence on the optical absorption, because it removes the doubly-degenerate excited state to give two optical absorption bands in the visible region. Our attention is therefore focused on the electronic characterization of representative phthalocyanines from the aspect of molecular distortion. We have recently recognized that the structure of MfPc determined by Robertson (1936) was perfect for an experimental set-up at that time, but not precise enough for the examination of molecular distortion. For this reason, the present structure determination was undertaken.

The crystal structure is basically in good agreement with the β phase reported by Robertson (1936). The molecule is slightly distorted at the four corners. Two of the phenyl rings are located below the molecular plane while the other two are raised above the plane by 1.9 (2) (C2, C3, C4, C5, C6, C7) and 2.3 (2)° (C10, C11, C12, C13, C14, C15), respectively. This leads to a molecular symmetry of C_i as opposed to D_{2h}, assumed for the free molecule. This small molecular deformation

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is big enough to lift the degeneracy of the excited state of MfPc and induces a significant influence on the optical absorption. The present molecular deformation, however, could not be observed in the structure of Robertson because of its high standard uncertainty. Table 1 details selected bond lengths and angles. No noticeable bond alternation is seen in the phenyl rings, whereas some bond alternations are clearly observed in the previous report (Robertson, 1936).

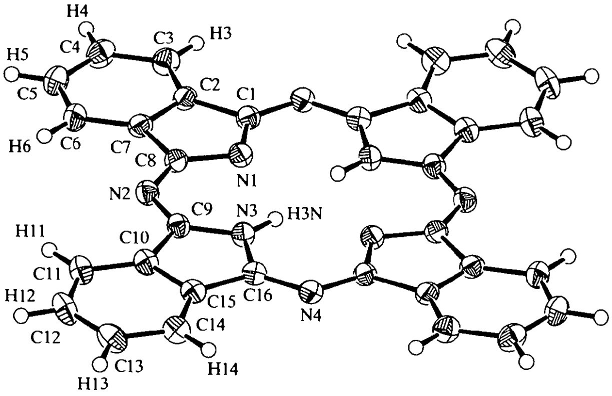

Fig. 1. The molecular conformation of MfPc showing 40% probability displacement ellipsoids for non-H atoms. H atoms are shown as spheres of an arbitrary radius.

Fig. 2 shows a packing diagram of the crystal structure. The molecules are stacked in a herringbone fashion along the *b* axis. The interplanar distance is about 3.31 Å and each molecular plane makes an angle of about 45° with the *b* axis.

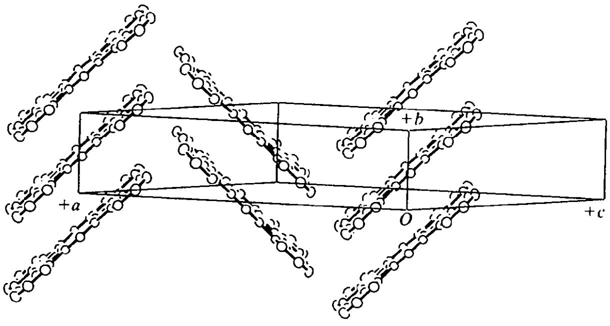

Fig. 2. Packing diagram of MfPc. H atoms are omitted for clarity.

Details of the influence of molecular distortion on the optical absorption will be reported elsewhere.

Experimental

Metal-free phthalocyanine was purchased from Fluka Chemicals and purified four times by sublimation. The single crystals were then grown from the vapor phase, using a two-zone furnace (Mizuguchi, 1981). A number of lustrous crystals were obtained after 24 h of vapor growth. The density of the single crystal was measured by flotation in carbon tetrachloride/toluene solution.

Crystal data

$C_{32}H_{18}N_8$
$M_r = 514.55$
Monoclinic
$P2_1/a$
$a = 19.870\,(7)$ Å
$b = 4.731\,(7)$ Å
$c = 14.813\,(7)$ Å
$\beta = 121.98\,(4)°$
$V = 1181\,(1)$ Å^3
$Z = 2$
$D_x = 1.447$ Mg m^{-3}
$D_m = 1.443$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 14.5\text{–}15.0°$
$\mu = 0.091$ mm^{-1}
$T = 296.2$ K
Prism
$0.80 \times 0.40 \times 0.10$ mm
Dark blue

Data collection

Rigaku AFC-7*R* diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.959$, $T_{\max} = 1.000$
3149 measured reflections
3037 independent reflections

1868 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 27.49°$
$h = -21 \rightarrow 25$
$k = -6 \rightarrow 0$
$l = -19 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: 0.94%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.059$
$S = 1.182$
1868 reflections
185 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o) + 0.00099|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: type 2 Gaussian isotropic Zachariasen (1967)
Extinction coefficient: 0.007 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C2—C3	1.383 (3)	C10—C11	1.392 (3)
C2—C7	1.395 (3)	C10—C15	1.399 (3)
C3—C4	1.387 (3)	C11—C12	1.380 (3)
C4—C5	1.392 (4)	C12—C13	1.399 (4)
C5—C6	1.387 (3)	C13—C14	1.380 (3)
C6—C7	1.391 (3)	C14—C15	1.389 (3)
C3—C2—C7	120.9 (2)	C11—C10—C15	121.6 (2)
C2—C3—C4	117.6 (2)	C10—C11—C12	117.4 (2)
C3—C4—C5	121.4 (2)	C11—C12—C13	121.1 (2)
C4—C5—C6	121.3 (2)	C12—C13—C14	121.6 (2)
C5—C6—C7	117.0 (2)	C13—C14—C15	117.7 (2)
C2—C7—C6	121.7 (2)	C10—C15—C14	120.6 (2)

All non-H atoms were refined anisotropically by full-matrix least-squares methods. The two H atoms of the NH groups were found in difference Fourier maps and their positional parameters were refined, whereas the other 16 H atoms were positioned geometrically and allowed to ride during the refinement.

Data collection: Rigaku/AFC diffractometer control software. Cell refinement: Rigaku/AFC diffractometer control software. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1066). Services for accessing these data are described at the back of the journal.

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