The molecular packing in the crystal is shown in Fig. 2. The molecules stack in the direction of the b axis. Pairs of hydrogen bonds occur between molecules of opposite configuration [$O(2)\cdots O(5)$ 2·723 (3), $O(2)\cdots H(7)$ 1·72 (5) Å, $O(2)\cdots H(7)-O(5)$ 174 (4)° and $O(4)\cdots O(1)$ 2·650 (3), $O(4)\cdots H(1)$ 1·65 (4) Å, $O(4)\cdots O(1)-H(1)$ 145 (4)°]. There are no other non-hydrogen contacts between molecules of less than 3·2 Å.

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Structure of Metal-Free Phthalocyanine Stabilized by the Addition of its 4-Chloro Derivative

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Abstract. 1:1 mixture of phthalocyanine ($C_{32}H_{18}N_8$) and 4-chlorophthalocyanine ($C_{32}H_{17}ClN_8$), averaged $M_r = 531$, monoclinic, $C2/n$, $a = 26\cdot460$ (1), $b = 3\cdot760$ (2), $c = 24\cdot275$ (1) Å, $\beta = 93\cdot53$ (1)°, $V = 2410\cdot2$ (2) Å^3, $Z = 4$, $D_m = 1\cdot47$, $D_x = 1\cdot465$ Mg m^{-3}. Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 7\cdot167$ mm^{-1}, averaged $F(000) = 548$, $T = 298$ K, final $R = 0\cdot065$ for 1076 independent reflections. The chlorinated molecules occupy the lattice sites at random. The substitution of an H with a Cl occurs at one of the four equivalent molecular sites of 4, 4', 12 and 12' with an equal probability for each. The molecule, therefore, looks like a 4,4',12,12'-tetrachloro derivative in projection. The occupancy of Cl at each site is one-eighth because of the mixing with non-chlorinated molecules in the ratio of 1:1.

Introduction. Phthalocyanine and some of its metal derivatives have at least two crystal forms, the α and β forms (Robertson, 1935, 1936; Brown, 1968a). The α form does not grow to a large enough size for X-ray structure analysis. It transforms into the stable β form by heat treatment or in some organic solvents (Moser & Thomas, 1963). The crystal structure of the α form has

been deduced from the resemblance of X-ray powder diffraction patterns to those of platinum phthalocyanine which exceptionally grows only in the α form (Brown, 1968b). A small amount of chlorinated

Table 1. *Final atomic parameters* (× 10⁴), *equivalent isotropic temperature factors* (Å²) *and occupancy factors*

$$B_{eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{13}ac\cos\beta).$$

	x	y	z	B_{eq}	Occu-pancy
C(1)	756 (2)	2757 (16)	862 (2)	3·951	1·0
C(2)	1292 (2)	3134 (16)	983 (2)	3·926	1·0
C(3)	1579 (3)	4479 (17)	1438 (2)	3·812	1·0
C(4)	2098 (3)	4415 (21)	1419 (3)	5·902	1·0
C(5)	2341 (3)	2965 (20)	967 (3)	5·716	1·0
C(6)	2050 (3)	1614 (18)	508 (3)	4·987	1·0
C(7)	1531 (2)	1750 (16)	527 (2)	4·163	1·0
C(8)	1122 (2)	553 (15)	139 (2)	3·932	1·0
C(9)	842 (2)	−1941 (16)	−703 (2)	4·062	1·0
C(10)	927 (2)	−3370 (15)	−1251 (2)	3·919	1·0
C(11)	1372 (3)	−3860 (18)	−1525 (3)	4·902	1·0
C(12)	1319 (3)	−5234 (20)	−2058 (3)	5·719	1·0
C(13)	839 (3)	−6138 (18)	−2300 (2)	5·305	1·0
C(14)	402 (3)	−5737 (16)	−2023 (2)	4·566	1·0
C(15)	453 (2)	−4282 (16)	−1490 (2)	4·109	1·0
C(16)	82 (2)	−3325 (16)	−1104 (2)	4·148	1·0
N(1)	412 (2)	3740 (13)	1212 (2)	4·122	1·0
N(2)	662 (2)	1207 (13)	348 (2)	3·847	1·0
N(3)	1211 (2)	−826 (14)	−350 (2)	4·250	1·0
N(4)	334 (2)	−1938 (13)	−639 (2)	3·914	1·0
Cl(4)	2432 (4)	5665 (36)	2026 (4)	4·215	1/8
Cl(12)	1866 (6)	−5584 (41)	−2341 (5)	5·228	1/8

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·44 (1)	C(1)–N(1)	1·33 (1)
C(1)–N(2)	1·38 (1)	C(2)–C(3)	1·40 (1)
C(2)–C(7)	1·41 (1)	C(3)–C(4)	1·38 (1)
C(4)–C(5)	1·42 (1)	C(4)–Cl(4)	1·74 (2)
C(5)–C(6)	1·41 (1)	C(6)–C(7)	1·38 (1)
C(7)–C(8)	1·46 (1)	C(8)–N(2)	1·37 (1)
C(8)–N(3)	1·33 (1)	C(9)–C(10)	1·46 (1)
C(9)–N(3)	1·33 (1)	C(9)–N(4)	1·36 (1)
C(10)–C(11)	1·40 (1)	C(10)–C(15)	1·39 (1)
C(11)–C(12)	1·39 (1)	C(12)–C(13)	1·41 (1)
C(12)–Cl(12)	1·65 (2)	C(13)–C(14)	1·38 (1)
C(14)–C(15)	1·41 (1)	C(15)–C(16)	1·44 (1)
C(16)–N(4)	1·38 (1)		

C(2)–C(1)–N(1)	123·0 (5)	C(2)–C(1)–N(2)	110·3 (5)
N(1)–C(1)–N(2)	126·7 (5)	C(1)–C(2)–C(3)	132·8 (6)
C(1)–C(2)–C(7)	106·7 (5)	C(3)–C(2)–C(7)	120·5 (6)
C(2)–C(3)–C(4)	117·6 (6)	C(3)–C(4)–C(5)	122·3 (7)
C(3)–C(4)–Cl(4)	115·0 (7)	C(5)–C(4)–Cl(4)	122·1 (7)
C(4)–C(5)–C(6)	120·0 (7)	C(5)–C(6)–C(7)	117·3 (6)
C(2)–C(7)–C(6)	122·5 (6)	C(2)–C(7)–C(8)	105·6 (5)
C(6)–C(7)–C(8)	131·9 (6)	C(7)–C(8)–N(2)	110·3 (5)
C(7)–C(8)–N(3)	122·1 (5)	N(2)–C(8)–N(3)	127·6 (5)
C(10)–C(9)–N(3)	123·7 (5)	C(10)–C(9)–N(4)	108·2 (5)
N(3)–C(9)–N(4)	128·1 (6)	C(9)–C(10)–C(11)	131·4 (6)
C(9)–C(10)–C(15)	106·6 (5)	C(11)–C(10)–C(15)	122·1 (6)
C(10)–C(11)–C(12)	116·8 (6)	C(11)–C(12)–C(13)	121·0 (7)
C(11)–C(12)–Cl(12)	112·1 (8)	C(13)–C(12)–Cl(12)	127·0 (8)
C(12)–C(13)–C(14)	122·2 (7)	C(13)–C(14)–C(15)	117·0 (6)
C(10)–C(15)–C(14)	120·9 (6)	C(10)–C(15)–C(16)	107·3 (5)
C(14)–C(15)–C(16)	131·7 (6)	C(15)–C(16)–N(4)	108·3 (5)
C(1)–N(2)–C(8)	107·1 (5)	C(8)–N(3)–C(9)	122·5 (5)
C(9)–N(4)–C(16)	109·6 (5)		

derivatives is added to some industrial products of phthalocyanines in order to avoid the color change due to particle growth in organic solvents. We have found that single crystals of phthalocyanine obtained by sublimation of such industrial materials are in the α form. This paper describes the structure of the α form of phthalocyanine and the function of the chlorine which inhibits the phase transformation.

Experimental. Some needle-like crystals several millimetres in length were obtained by sublimation of the sample powder at about 823 K in nitrogen gas flow under reduced pressure. The sample was obtained from Tokyo Chemical Industry Co. Ltd. It was known to include chlorine. Energy-dispersive X-ray (EDX) analysis and elemental analysis revealed the existence of the chlorine in the crystals. Mass spectroscopy proved that they were composed of pure metal-free phthalocyanine and its monochlorinated derivative in the ratio 1:1.

Crystal dimensions 0·8 × 0·1 × 0·05 mm, D_m by flotation in CCl_4–benzene mixture. Rigaku automated four-circle diffractometer (AFC-5), graphite-monochromated Cu $K\alpha$; cell constants determined by least-squares procedure for 36 reflections; intensity data by ω-scan mode, $2\theta_{max} = 120°$, intensity variation of standard reflections (004, 11$\bar{3}$ and $\bar{1}$1$\bar{3}$) within ±0·9%, 1557 independent reflections in the range $0 \le h \le 27$, $0 \le k \le 4$, $-26 \le l \le 26$.

Lp corrections but not absorption; 1076 reflections with $|F_o| > 3\sigma(|F_o|)$; structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); all C and N atoms from E map; refinement on F by least squares; H and Cl atoms from difference Fourier map; several Cl
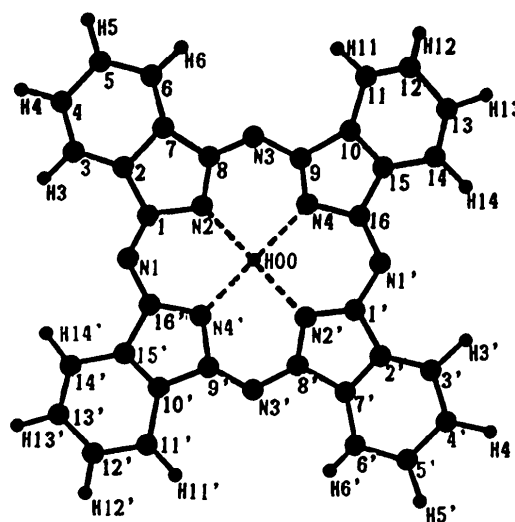

Fig. 1. Numbering of atoms in the molecule. The chemical symbol for the C atoms has been omitted. H atoms have the same numbers as the carbons to which they are attached.

occupancies (2^{-n}, $n = 1$, 2, 3, 4) were introduced, lowest R and reasonable isotropic temperature factors of Cl were obtained as 0·068 and 3·7–5·1, respectively, for $n = 3$; two H atoms at the center of the molecule were treated with a split-atom model, they located at the molecular center and four sites binding to N; each occupancy was 2/5; $w = 1$ for $|F_o| > 0$ reflections, $w = 0.5$ for $|F_o| = 0$; final $R = 0.065$, $wR = 0.060$ with anisotropic temperature factors except for H; max. $\Delta/\sigma = 0.008$ for C and N, 0·015 for Cl; residual electron density in final difference map $-0.5 \leq \rho \leq 0.5$ e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); all the numerical computations were made on an ACOS series 77–700 computer of the Crystallographic Research Center, Institute for Protein Research, Osaka Univ., using *HBLS*-V in *UNICS* (1979).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1* with the site occupancies. Bond distances and angles

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44511 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
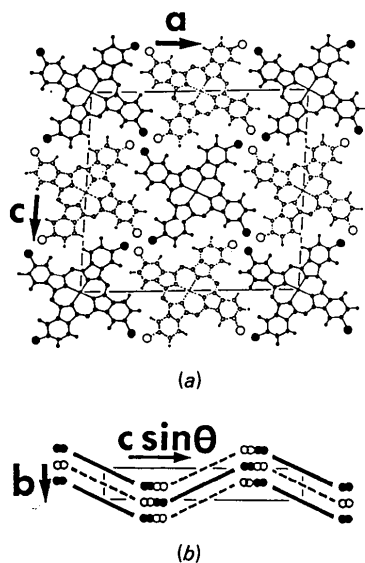

(a)

(b)

Fig. 2. (a) The projection of the unit cell along the b axis and (b) along the a axis. The equivalent positions in space group $C2/n$ are $\pm(x, y, z; x, \frac{1}{2}-y, \frac{1}{2}+z; \frac{1}{2}+x, -y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}+y, z)$. Small circles C and N, large circles Cl, dots H. Molecules represented by straight lines and full circles are located on the (010) (a) and (100) (b) planes. In (b), the porphyrin rings are drawn as rods and the Cl atoms are large full or open circles. The molecules represented by the dotted lines and open circles are on the planes half a period above or below the projected direction.

are listed in Table 2. The atomic numbering of the molecule is shown in Fig. 1. The larger values for the y coordinates of atoms and bond distances and angles along the b axis might be due to the anisotropic cell parameters. The number of reflections in calculation along the b axis is less than that along the a and c axes.

The structure is isomorphic with that of platinum(II) phthalocyanine in the α form (Brown, 1968b). Any extra diffraction spots due to pairing or the ordered sequence of packing of non- and monochlorinated molecules were not observed. That is, there are no definite lattice sites for the chlorinated molecules and they mix quite at random with non-chlorinated ones in the crystal.

The substitution of a hydrogen with a chlorine may occur at the eight chemically equivalent positions 4,5,12,13,4′,5′,12′ and 13′ on the molecule. However, it appears that only the sites 4,4′,12 and 12′ are occupied in the crystal with the same probability. Molecules substituted at the 5,5′,13 or 13′ sites by a chlorine turn inside out to become the 4,4′,12 or 12′-monochlorinated versions in the crystal. After averaging over all molecules in the crystal the molecule looks like 4,4′,12,12′-tetrachlorophthalocyanine in projection. Figs. 2(a) and 2(b) show the packing of molecules viewed along the b and a axes, respectively. The molecule is planar and the deviations of atoms from the least-squares plane are within ±0·05 (1) Å for all C and N and ±0·020 (2) Å for Cl. The plane makes an angle of 23·3° with the b axis and the mean intermolecular distance is 3·44 (1) Å along the plane normal.

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