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Crystal structure of 2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyanine - trichloromethane (1/2), $C_{98}H_{84}Cl_6N_8O_8$

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.10 × 0.08 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	2.28 mm ⁻¹
Diffractometer, scan mode:	APEX, ω and ϕ scans
$\theta_{\max}$, completeness:	63.5°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14028, 7069, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5641
$N(\text{param})_{\text{refined}}$:	554
Programs:	Bruker [1, 3], SHELX [2]

The crystal structure is shown in the figure. The non-hydrogen atoms of the asymmetric unit are labeled. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

n-Pentanol and *n*-octanol were distilled from sodium under nitrogen. Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. All other reagents and solvents were used as received. 2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyanine was prepared according to the literature procedures with slight modification [4]. 4,5-Dichlorophthalonitrile (4.0 g, 20 mmol) and 2,6-dimethylphenol (14.6 g, 120 mmol) in dry DMSO (40 mL) were stirred under dry nitrogen at 95 °C. Dry potassium carbonate (60 g) was added (in 5 min) and the solution was stirred at 95 °C for an additional 1.5 h, then cooled and poured into ice-water (400 mL). The sticky precipitate was filtered, washed with cold water, ethanol, and then dissolved in trichloromethane and precipitated with ethanol with subsequent evaporation of dichloromethane. The precipitate was filtered and vacuum-dried to get the 4,5-bis(2,6-dimethylphenoxy)phthalonitrile. Then the bis(diiminoisoindoline) (prepared from the 101 mg (0.57 mmol) 1,2,4,5-tetra-cyanobenzene) and 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (1.4 g, 4 mmol) were added to the *n*-BuOH (40 mL) solution and the mixture was

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Abstract

$C_{98}H_{84}Cl_6N_8O_8$, triclinic, $P\bar{1}$ (no. 2), $a = 8.3431(3)$ Å, $b = 16.1109(6)$ Å, $c = 18.1405(7)$ Å, $\alpha = 109.242(4)^\circ$, $\beta = 95.119(3)^\circ$, $\gamma = 103.798(3)^\circ$, $V = 2197.92(16)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0595$, $wR_{\text{ref}}(F^2) = 0.1689$, $T = 293(2)$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	−0.1555(2)	0.29448(12)	0.72314(11)	0.0247(4)
N1	0.5431(3)	0.60934(16)	0.60052(15)	0.0235(5)
C1	0.4743(3)	0.60477(18)	0.66491(16)	0.0221(6)
H1	0.522(4)	0.570(2)	0.558(2)	0.031(9)*
O2	−0.2205(2)	0.15334(13)	0.59084(11)	0.0282(5)
N2	0.3595(3)	0.53648(15)	0.67115(13)	0.0230(5)
C2	0.2965(3)	0.45500(18)	0.61243(16)	0.0214(6)
O3	0.1971(3)	0.04385(13)	0.12218(11)	0.0287(5)
N3	0.3465(3)	0.42391(15)	0.54137(13)	0.0223(5)
C3	0.1606(3)	0.38431(18)	0.61993(16)	0.0220(6)
O4	0.3897(3)	0.14863(13)	0.06637(11)	0.0294(5)
N4	0.2539(3)	0.27817(15)	0.43062(13)	0.0233(5)
C4	0.0650(3)	0.38415(18)	0.67917(16)	0.0228(6)
H4	0.0835	0.4359	0.7248	0.027*
C5	−0.0576(3)	0.30472(19)	0.66749(16)	0.0218(6)
C6	−0.0888(3)	0.22660(18)	0.59694(16)	0.0233(6)
C7	0.0069(3)	0.22754(18)	0.53856(16)	0.0236(6)
H7	−0.0122	0.1764	0.4924	0.028*
C8	0.1330(3)	0.30782(18)	0.55144(16)	0.0216(6)
C9	0.2500(3)	0.33499(18)	0.50298(16)	0.0219(6)
C10	0.3475(3)	0.30574(18)	0.38343(16)	0.0212(6)
C11	0.3473(3)	0.25114(18)	0.30185(16)	0.0218(6)
C12	0.2582(4)	0.16098(18)	0.25422(16)	0.0238(6)
H12	0.1880	0.1231	0.2744	0.029*
C13	0.2783(4)	0.13045(18)	0.17634(17)	0.0248(6)
C14	0.3835(4)	0.18815(19)	0.14503(16)	0.0229(6)
C15	0.4729(3)	0.27647(18)	0.19220(16)	0.0229(6)
H15	0.5434	0.3143	0.1721	0.028*
C16	0.4535(3)	0.30713(18)	0.27161(16)	0.0226(6)
C17	−0.1900(4)	0.37306(19)	0.77348(17)	0.0268(6)
C18	−0.3363(4)	0.3907(2)	0.7497(2)	0.0354(7)
C19	−0.3789(5)	0.4641(2)	0.8012(2)	0.0469(9)
H19	−0.4774	0.4771	0.7869	0.056*
C20	−0.2756(5)	0.5178(2)	0.8733(2)	0.0515(10)
H20	−0.3047	0.5670	0.9074	0.062*
C21	−0.1293(5)	0.4991(2)	0.8950(2)	0.0431(9)
H21	−0.0603	0.5366	0.9435	0.052*
C22	−0.0826(4)	0.4253(2)	0.84595(17)	0.0318(7)
C23	0.0716(5)	0.4022(2)	0.87151(19)	0.0419(8)
H23A	0.1452	0.4545	0.9139	0.063*
H23B	0.1282	0.3853	0.8274	0.063*
H23C	0.0401	0.3518	0.8895	0.063*
C24	−0.4450(5)	0.3325(3)	0.6696(2)	0.0513(10)
H24A	−0.5593	0.3330	0.6718	0.077*
H24B	−0.4381	0.2707	0.6555	0.077*
H24C	−0.4066	0.3566	0.6304	0.077*
C25	−0.2718(4)	0.0798(2)	0.51717(18)	0.0288(7)
C26	−0.2391(4)	−0.0020(2)	0.51448(19)	0.0316(7)
C27	−0.2946(4)	−0.0757(2)	0.4425(2)	0.0402(8)
H27	−0.2753	−0.1314	0.4384	0.048*
C28	−0.3779(4)	−0.0676(2)	0.3771(2)	0.0451(9)
H28	−0.4121	−0.1173	0.3292	0.054*
C29	−0.4102(4)	0.0138(2)	0.3826(2)	0.0419(8)
H29	−0.4679	0.0182	0.3384	0.050*
C30	−0.3583(4)	0.0899(2)	0.45322(19)	0.0343(7)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C31	−0.3983(5)	0.1777(2)	0.4590(2)	0.0447(8)
H31A	−0.4425	0.1997	0.5065	0.067*
H31B	−0.4800	0.1668	0.4136	0.067*
H31C	−0.2979	0.2228	0.4606	0.067*
C32	−0.1521(4)	−0.0109(2)	0.5857(2)	0.0406(8)
H4A1	−0.2048	0.0115	0.6302	0.061*
H4A2	−0.0363	0.0242	0.5976	0.061*
H4A3	−0.1592	−0.0742	0.5752	0.061*
C33	0.1221(4)	−0.02066(18)	0.15373(16)	0.0260(6)
C34	0.2211(4)	−0.0691(2)	0.17681(17)	0.0305(7)
C35	0.1459(5)	−0.1343(2)	0.2065(2)	0.0426(8)
H35	0.2080	−0.1686	0.2219	0.051*
C36	−0.0207(5)	−0.1488(2)	0.2134(2)	0.0461(9)
H36	−0.0689	−0.1920	0.2345	0.055*
C37	−0.1170(4)	−0.1007(2)	0.1897(2)	0.0430(9)
H37	−0.2294	−0.1120	0.1947	0.052*
C38	−0.0472(4)	−0.0348(2)	0.15812(19)	0.0332(7)
C39	−0.1476(5)	0.0175(3)	0.1289(2)	0.0507(10)
H39A	−0.2575	0.0044	0.1420	0.076*
H39B	−0.1571	−0.0004	0.0724	0.076*
H39C	−0.0923	0.0821	0.1537	0.076*
C40	0.4037(4)	−0.0495(2)	0.1696(2)	0.0436(8)
H5A1	0.4507	−0.0924	0.1835	0.065*
H5A2	0.4631	0.0117	0.2047	0.065*
H5A3	0.4135	−0.0554	0.1159	0.065*
C41	0.4579(4)	0.20785(19)	0.02816(16)	0.0247(6)
C42	0.6239(4)	0.2188(2)	0.01890(17)	0.0318(7)
C43	0.6856(4)	0.2739(2)	−0.0232(2)	0.0424(8)
H43	0.7963	0.2828	−0.0307	0.051*
C44	0.5850(5)	0.3156(2)	−0.0540(2)	0.0440(9)
H44	0.6281	0.3522	−0.0820	0.053*
C45	0.4200(4)	0.3030(2)	−0.04332(19)	0.0382(8)
H45	0.3529	0.3311	−0.0646	0.046*
C46	0.3529(4)	0.2492(2)	−0.00138(17)	0.0294(7)
C47	0.1736(4)	0.2340(2)	0.0111(2)	0.0397(8)
H47A	0.1129	0.2557	−0.0225	0.059*
H47B	0.1714	0.2668	0.0656	0.059*
H47C	0.1222	0.1697	−0.0018	0.059*
C48	0.7296(5)	0.1712(3)	0.0518(2)	0.0532(10)
H48A	0.8373	0.1822	0.0361	0.080*
H48B	0.6749	0.1064	0.0316	0.080*
H48C	0.7443	0.1944	0.1087	0.080*
C49	0.9318(6)	0.3612(3)	0.3093(3)	0.0631(12)
H49	0.8332	0.3791	0.2942	0.076*
Cl1	1.0711(2)	0.37556(13)	0.24635(12)	0.1074(6)
Cl2	1.0213(3)	0.42992(13)	0.40712(9)	0.1453(10)
Cl3	0.86685(17)	0.24623(10)	0.29942(9)	0.0835(4)

heated under reflux for 48 h. After the reaction mixture had been cooled, methanol (200 mL) was added and the resulting mixture was stirred for 1 h. The precipitate was collected by the centrifugation, washed with methanol, dried and then extracted with toluene. After evaporation of toluene the solid

was dissolved in trifluoroacetic acid (25 mL) and stirred in the dark for 1 h. The solution was poured into ice-water (100 mL) the precipitate collected, washed successively with water, 5% $NaHCO_3$, water and methanol, then dried under vacuum, extracted with toluene/hexanes (4:1 v/v) and subjected to chromatography on silica gel eluting with toluene/hexanes gradually reducing the hexanes content from 20 to 50 vol%. From the first green fraction containing 2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninate the solvents were evaporated and the resulting solid was recrystallised from the toluene and trichloromethane. (0.36 g, 24%). 1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.18(s, 8H), 7.30–7.41(brm, 24H), 2.43(s, 48H) – 0.76 ppm(brs, 2H); IR(KBr): 3296(N–H), 3024, 2952, 2922, 2854, 1612, 1588, 1442, 1396, 1328, 1276, 1222, 1188, 1092, 1016, 920, 878, 834, 800, 762, 708, 696 cm^{-1} .

Experimental details

Hydrogen atoms were added using a riding model implemented in the crystallographic software [2, 3].

Comment

Some of the most important applications of phthalocyanines (Pcs) are based on the interaction of visible light with the chromophores of these molecules: dyes and pigments, photoconductors in laser printers, photosensitisers in the photodynamic therapy of cancer and degradation of pollutants of waste and natural water [5–12]. Pcs as thin films or adsorbed on inorganic semiconductors have potential applications in photovoltaic or dye-sensitised solar cells. Based on these applications and taking into account the increasing interest in near-infrared (NIR) absorbing systems, it is important to synthesize compounds with absorptions over a broad region of visible light down to the NIR region. The similar phthalocyanine 2,3,9,10,16,17,23,24-octakis(2-tetrahydropyran)phthalocyanine has been reported [13].

The figure depicts a perspective drawing of the compound showing the atom numbering. The atoms of the phthalocyaninate ring are in the same plane, the 2,6-dimethylphenoxy group is almost vertical to the phthalocyaninate ring.

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