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Crystal and molecular structures of metal-free phthalocyanines, 1,2-dicyanobenzene tetramers
II. α form

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Abstract

The α polymorph of 1,2-dicyanobenzene tetramer (α-Pc) has been obtained in the reaction of 1,2-dicyanobenzene in presence of InBi alloy. α-Pc crystallizes in the monoclinic system, (space group, $C2/n$). The unit-cell parameters are $a=26.124(3)$ Å, $b=3.801(1)$ Å, $c=23.889(3)$ Å, $\beta=94.18(2)°$ and $V=2365.8(6)$ Å^3. The unit cell contains four centrosymmetrical molecules. A total of 3934 reflections was used in solution and refinement. The final values were $R=0.0577$, $\omega R=0.0742$ and $S=1.65$. The crystal structure of α-Pc is discussed and compared with the β modification of phthalocyanine.

1. Introduction

In the previous paper, Part I [1], we stated that 1,2-dicyanobenzene heated at 210 °C in vacuum in the presence of $AuSn_4$ alloy partially undergoes tetramerization, forming the β form of phthalocyanine (β-Pc). In this paper we present the crystal structure of the α polymorph of phthalocyanine (α-Pc). α-Pc was obtained in the same reaction conditions using InBi alloy with 1,2-dicyanobenzene. It was found that there were two types of violet crystal present in the reaction products. An analysis of the elements made on an energy-dispersive spectrometer showed the presence of indium in one type of these crystals. This crystal type was identified as In_2Pc_3 (the crystal structure of this compound will be published later). The crystals of the second type were metal free and had been identified (from Weissenberg photographs) as isomorphic with the known α form of platinum phthalocyanine [2]. Taking into account the data from ref. 1, we assumed that in this case it should be an α form of the 1,2-dicyanobenzene tetramer, *i.e.* α-Pc. However, from the literature it was known that the α polymorph of metallphthalocyanines were less stable than the β polymorph [2–4]. Certainly this is a reasonable explanation for the fact that structural data on the α form of metal-free phthalocyanines has not yet appeared. Moreover until now it was believed that metal-free phthalocyanines possess only the H_2Pc-type composition and phthalocyanine must be an anion and therefore unstable [5]. The following facts enabled us to perform the crystal structure determination on the single crystals.

2. Experimental details

2.1. Preparation

The crystals were obtained by reaction of InBi alloy with 1,2-dicyanobenzene in the mass proportions 1:1. Filings of InBi were mixed together with 1,2-dicyanobenzene, pressed into a pellet and heated in an evacuated and sealed glass tube at 210 °C for 1 week.

2.2. Crystal data

The crystal data are as follows:

$C_{32}H_{16}N_8$; $M_r=512.5$; monoclinic system; space group, $C2/n$; $a=26.124(3)$ Å, $b=3.801(1)$ Å and $c=23.889(3)$ Å; $\beta=94.18(2)°$; $V=2365.8(6)$ Å^3; $Z=4$; $D_0=1.43$ g cm^{-3}; $D_c=1.439$ g cm^{-3}; λ(Cu Kα)$=1.54056$ Å; μ(Cu Kα)$=6.82$ cm^{-1}; $F(000)=1056$; $T=300$ K.

A crystal of approximate dimensions 0.18 mm×0.18 mm×0.30 mm was used for data collection on a four-circle Kuma Diffraction KM-4 diffractometer with graphite-monochromated Cu Kα radiation. Initially the crystal was examined by rotation, and Weissenberg photographs revealed the following systematic absences: hkl where $h+k=2n+1$; $h0l$ where $h+l=2n+1$. The systematic absences indicated a space group of $C2/n$ and this was used in the crystal solution and refinement. The lattice parameters were

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refined by the least-squares method fit of 20 reflections measured in the range $20° \leqslant 2\vartheta \leqslant 25°$. 3934 reflections were measured in the range $4° \leqslant 2\vartheta \leqslant 164°$ ($[\sin\theta/\lambda]_{max} = 0.643$) using the ω–2ϑ scan technique with scan speed of 0.03–0.1° s^{-1} and a scan width of 1.4°. The *hkl* range was as follows: h, $-28 \rightarrow 28$; k, $0 \rightarrow 4$, $l - 26 \rightarrow 26$. Two standard reflection ((6012) and ($80\bar{6}$)) were monitored every 50 reflections; the intensity varied less than 1%. The measured intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. 2239 unique reflection (1475 with $F > 4\sigma_F$; $R_{int} = 0.044$) were used in calculations.

2.3. *Structure determination*

The structure was solved by the direct method with the SHELXTL program system [6]. The hydrogen atoms were located from difference Fourier synthesis. The structure was refined by the full-matrix least-squares method with anisotropic temperature factors for carbon and nitrogen atoms and isotropic factors for hydrogen atoms. An empirical secondary extinction correction was applied according to the formula $F_{cor} = F(1 + 0.002\kappa F^2/\sin\vartheta)^{-1/4}$ where κ converged to 0.0009(4). The function minimized was $\Sigma(|F_o| - |F_c|)^2$ with $\omega = (\sigma_F^2 + 0.001F^2)^{-1}$. The final values were $R = 0.0577$, $\omega R = 0.0742$ and $S = 1.65$ for 214 refined parameters, $(\Delta/\sigma)_{max} = 0.029$. The residual electron density in the final difference Fourier map was −0.16–0.87 electrons $Å^{-3}$. The atomic scattering factors were as supplied by the SHELXTL program. All calculations were performed on an IBM PC/AT. The final atomic parameters are given in Table 1, and the bond lengths and angles are collected in Table 2.

TABLE 1. Atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{eq}[a]
N(1)	0.04116(10)	0.38444(76)	0.12259(10)	0.0489(9)
N(2)	0.06717(10)	0.12566(73)	0.03648(10)	0.0491(9)
N(3)	0.12279(10)	−0.08248(78)	−0.03365(10)	0.0496(9)
N(4)	0.03363(10)	−0.19838(80)	−0.06378(10)	0.0497(9)
C(1)	0.07575(12)	0.28224(91)	0.08792(12)	0.0472(10)
C(2)	0.13074(12)	0.32123(88)	0.10076(13)	0.0479(10)
C(3)	0.16004(14)	0.46198(106)	0.14654(14)	0.0568(12)
C(4)	0.21231(14)	0.45575(114)	0.14542(16)	0.0629(13)
C(5)	0.23563(14)	0.31307(116)	0.10042(17)	0.0646(13)
C(6)	0.20727(14)	0.17338(110)	0.05464(15)	0.0581(12)
C(7)	0.15465(11)	0.18164(91)	0.05558(12)	0.0480(10)
C(8)	0.11380(11)	0.05995(95)	0.01523(12)	0.0475(10)
C(9)	0.08564(11)	−0.19758(94)	−0.07012(12)	0.0469(10)
C(10)	0.09478(12)	−0.34374(87)	−0.12424(13)	0.0482(10)
C(11)	0.13886(14)	−0.39196(100)	−0.15235(16)	0.0569(12)
C(12)	0.13384(15)	−0.53561(116)	−0.20588(16)	0.0639(13)
C(13)	0.08608(15)	−0.62787(109)	−0.23124(16)	0.0626(13)
C(14)	0.04176(14)	−0.58510(94)	−0.20326(13)	0.0539(11)
C(15)	0.04689(12)	−0.43930(91)	−0.14969(13)	0.0479(10)
C(16)	0.00851(12)	−0.34161(90)	−0.11113(12)	0.0469(10)
H(3)	0.1430(14)	0.5578(119)	0.1743(17)	0.068(12)
H(4)	0.2324(17)	0.5621(135)	0.1812(21)	0.099(15)
H(5)	0.2707(12)	0.3183(111)	0.0999(16)	0.070(12)
H(6)	0.2218(12)	0.0518(103)	0.0240(14)	0.051(9)
H(11)	0.1730(14)	−0.3260(104)	−0.1376(14)	0.061(11)
H(12)	0.1661(14)	−0.5854(116)	−0.2271(18)	0.080(13)
H(13)	0.0821(14)	−0.7185(123)	−0.2743(18)	0.078(12)
H(14)	0.0064(15)	−0.6443(108)	−0.2247(15)	0.073(12)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Bond lengths and angles with estimated standard deviations in parentheses

Bond length (Å)			
N(1)–C(1)	1.328(4)	N(1)–C(16A)	1.317(4)
N(2)–C(1)	1.369(4)	N(2)–C(8)	1.376(4)
N(3)–C(8)	1.324(4)	N(3)–C(9)	1.330(4)
N(4)–C(9)	1.378(4)	N(4)–C(16)	1.378(4)
C(1)–C(2)	1.454(4)	C(2)–C(3)	1.395(5)
C(2)–C(7)	1.391(4)	C(3)–C(4)	1.368(5)
C(3)–H(3)	0.902(41)	C(4)–C(5)	1.384(6)
C(4)–H(4)	1.051(47)	C(5)–C(6)	1.382(5)
C(5)–H(5)	0.918(32)	C(6)–C(7)	1.377(5)
C(6)–H(6)	0.967(36)	C(7)–C(8)	1.460(4)
C(9)–C(10)	1.443(4)	C(10)–C(11)	1.387(5)
C(10)–C(15)	1.398(4)	C(11)–C(12)	1.388(5)
C(11)–H(11)	0.967(35)	C(12)–C(13)	1.392(5)
C(12)–H(12)	1.032(41)	C(13)–C(14)	1.388(5)
C(13)–H(13)	1.083(43)	C(14)–C(15)	1.392(4)
C(14)–H(14)	1.047(38)	C(15)–C(16)	1.458(4)
C(16)–N(1A)	1.317(4)		
Bond angle (deg)			
C(1)–N(1)–C(16A)	122.6(3)	C(1)–N(2)–C(8)	108.6(2)
C(8)–N(3)–C(9)	123.0(3)	C(9)–N(4)–C(16)	109.0(2)
N(1)–C(1)–N(2)	127.8(3)	N(1)–C(1)–C(2)	123.1(3)
N(2)–C(1)–C(2)	109.2(3)	C(1)–C(2)–C(3)	133.0(3)
C(1)–C(2)–C(7)	106.9(3)	C(3)–C(2)–C(7)	120.2(3)
C(2)–C(3)–C(4)	118.0(3)	C(2)–C(3)–H(3)	117.3(24)
C(4)–C(3)–H(3)	124.6(24)	C(3)–C(4)–C(5)	121.2(3)
C(3)–C(4)–H(4)	114.8(26)	C(5)–C(4)–H(4)	124.0(27)
C(4)–C(5)–C(6)	121.6(3)	C(4)–C(5)–H(5)	119.9(25)
C(6)–C(5)–H(5)	118.5(25)	C(5)–C(6)–C(7)	117.2(3)
C(5)–C(6)–H(6)	124.4(19)	C(7)–C(6)–H(6)	118.1(19)
C(2)–C(7)–C(6)	121.8(3)	C(2)–C(7)–C(8)	106.6(3)
C(6)–C(7)–C(8)	131.7(3)	N(2)–C(8)–N(3)	128.2(3)
N(2)–C(8)–C(7)	108.8(3)	N(3)–C(8)–C(7)	122.9(3)
N(3)–C(9)–N(4)	127.4(3)	N(3)–C(9)–C(10)	123.6(3)
N(4)–C(9)–C(10)	109.1(3)	C(9)–C(10)–C(11)	133.0(3)
C(9)–C(10)–C(15)	106.8(3)	C(11)–C(10)–C(15)	120.2(3)
C(10)–C(11)–C(12)	118.2(3)	C(10)–C(11)–H(11)	124.4(22)
C(12)–C(11)–H(11)	117.4(22)	C(11)–C(12)–C(13)	121.4(4)
C(11)–C(12)–H(12)	119.9(22)	C(13)–C(12)–H(12)	118.6(23)
C(12)–C(13)–C(14)	120.9(3)	C(12)–C(13)–H(13)	121.0(20)
C(14)–C(13)–H(13)	118.0(20)	C(13)–C(14)–C(15)	117.5(3)
C(13)–C(14)–H(14)	118.4(21)	C(15)–C(14)–H(14)	123.9(21)
C(10)–C(15)–C(14)	121.7(3)	C(10)–C(15)–C(16)	107.1(3)
C(14)–C(15)–C(16)	131.1(3)	N(4)–C(16)–C(15)	108.1(3)
N(4)–C(16)–N(1A)	128.5(3)	C(15)–C(16)–N(1A)	123.3(3)

3. Description of the structure and discussion

The molecular geometry and numbering of the atoms used in this paper are shown in Fig. 1. There are four centrosymmetrical molecules in the unit cell. A view of the stereopacking of the unit-cell content is shown in Fig. 2.

α-Pc is planar, similar to β-Pc [1]. The equation of the mean plane through the tetramer, referred to standard orthogonal axes, is $-0.0538X+0.8953Y-0.4423Z=0$. The mean displacement of the carbon, nitrogen and hydrogen atoms from this plane is 0.0102 Å, randomly below and above. The normal of the plane in the α polymorph makes an angle of 26.45° [2] and is smaller than that in the β form [1]. The perpendicular distance between successive planes of α-Pc molecules along the b axis is 3.403 Å and much smaller than that in β form (3.318 Å). The angle between two molecules of α-Pc planes is 126.9° and is greater than this angle in the β-Pc form (88.5°). The mutual arrangement of α-Pc molecules are shown in Fig. 3.

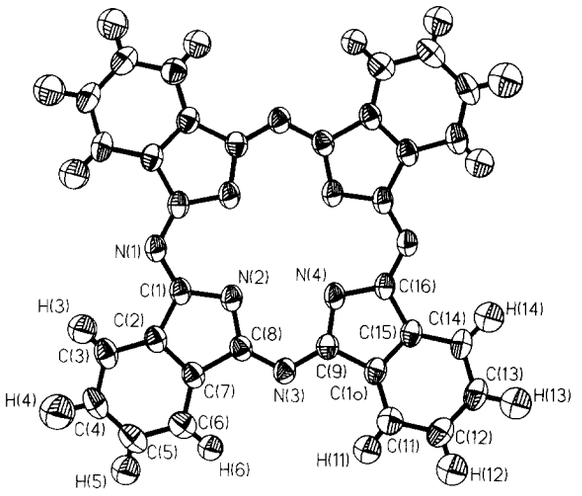

Fig. 1. A view of the molecule with the atomic numbering scheme.

No great accuracy is claimed for these bond and interbond angles between the α-Pc and β-Pc. The mean C–C distances found in the benzene rings are 1.387 Å, the mean C–C distances in the isoindole rings 1.454 Å (indicating that the bond order is 1.25 and therefore obviously linked with the π-electron-resonating system), the mean C–N distances in isoindole rings are 1.375 Å, and the mean C–N distances between the isoindole rings are 1.325 Å in α-Pc and 1.392, 1.455, 1.374 and 1.327 Å in β-Pc [1]. The interatomic distances N(2)–N(4) and N(2)–N(4)^i (where $i \equiv -x, -y, -z$) in the phthalocyanine rings are 2.779 and 2.772 Å in α-Pc and 2.828 and 2.713 Å in β-Pc. The short differences in the distances are relevant to the difference in the angle C–N–C between and in the isoindole rings. The angle C–N–C in the isoindole ring is 123.0°, and the angles between the isoindole ring are 122.6° in α-Pc and 123.8 and 121.8° in β-Pc.

A significant difference between the two (α and β) polymorphs is the angle between the normal of the planar molecule and the column direction (b axis). The degree of overlap of adjacent molecules in α-Pc is larger than in β-Pc and is therefore different in these molecular columns. The interaction between the phthalocyanine molecules in the β-form is stronger than in the α-form. It is caused by the existence of very weak hydrogen bonding between the molecules in β-Pc.

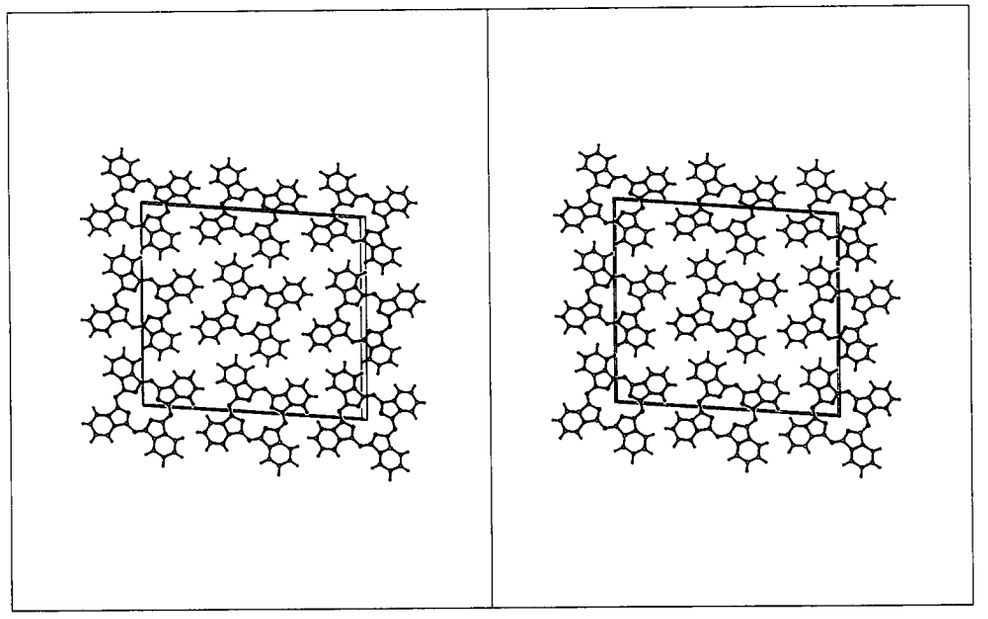

Fig. 2. Stereopacking of the phthalocyanine molecules in a unit cell.

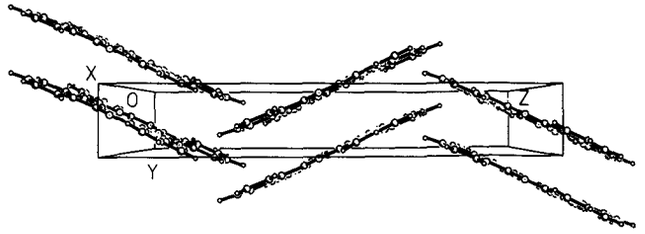

Fig. 3. The arrangement of the molecules in the unit cell.

The highest residual electron density (+0.87) has a position 0.0013 −0.03030 0.0107 in the $\Delta\rho$ map and is outside the phthalocyanine plane. The displacement of the highest maximum from the phthalocyanine plane is 1.153 Å and is 2.15 Å and 2.06 Å from the nearest $N(2)^i$ and N(4) atoms respectively and 2.42 and 2.50 Å from the second-nearest N(2) and $N(4)^i$ atoms respectively. It is very likely that the residual electron density arises from metal inclusions, which may stabilize the α form. We found that inserting bismuth atoms in that position gave quite reasonable bonds. The occupation factor of bismuth atoms in this position converged to 0.0096(5) (*i.e.* 0.077(4) bismuth atoms per unit cell); the residual electron density in the $\Delta\rho$ map dropped to −0.17–0.23 R to 0.0463 and ωR to 0.0564.

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