Redetermination of the crystal structure of α-copper phthalocyanine grown on KCl

**Akitaka Hoshino,* Yoshiko
Takenaka and Hideki Miyaji**

Department of Physics, Graduate School of
Science, Kyoto University, Japan

Correspondence e-mail:
hoshino@scphys.kyoto-u.ac.jp

The crystal structure of a polymorph of copper phthalocyanine (CuPc) grown on a KCl substrate is redetermined by transmission electron diffraction. It has a triclinic unit cell containing one molecule; the crystal does not have a herringbone-type molecular arrangement, which is a common packing mode of planar phthalocyanines. The molecular packing is determined by the diffraction intensity with the aid of the calculation of molecular packing energy. One of the striking features of this polymorph is its stacking mode within a molecular column: the molecular stacking direction projected on a molecular plane is different by an angle of about 45° from that of the α-modifications of platinum phthalocyanine (PtPc) and metal-free phthalocyanine (H_2Pc). A powder X-ray diffraction profile calculated for the polymorph agrees well with that of so-called α-CuPc and Rietveld analysis for α-CuPc indicates that the CuPc crystals grown on KCl are actually α-CuPc; hence, α-CuPc is not isostructural with either α-PtPc or α-H_2Pc. On the basis of the present results and the reported crystal structures of the planar phthalocyanines that form molecular columns, the polymorphs of the phthalocyanines can be classified into four types distinguished by the molecular stacking mode within the column: $\alpha(\times)$-, $\alpha(+)$-, $\beta(\times)$- and $\beta(+)$-types.

1. Introduction

Planar phthalocyanines such as metal-free phthalocyanine (H_2Pc) and copper phthalocyanine (CuPc) are known to crystallize into various structures (polymorphs); α-, β-, γ-, δ-, ε-, π-, τ-, χ- and M-modifications have been reported so far (McKeown, 1998, and references therein; Moser & Thomas, 1983, and references therein). Among them, the α- and β-modifications are well known; both structures consist of molecular columns, with a herringbone-type arrangement between the columns (Fig. 1). One of the significant differences between the α- and β-modifications is the overlapping of neighbouring molecules within a molecular column; the α-modification has a larger overlap and hence the lattice constant along the column direction, *i.e. b*, is shorter than that of the β-modification: b is typically approximately 3.8 Å for the α-modification and 4.8 Å for the β-modification.
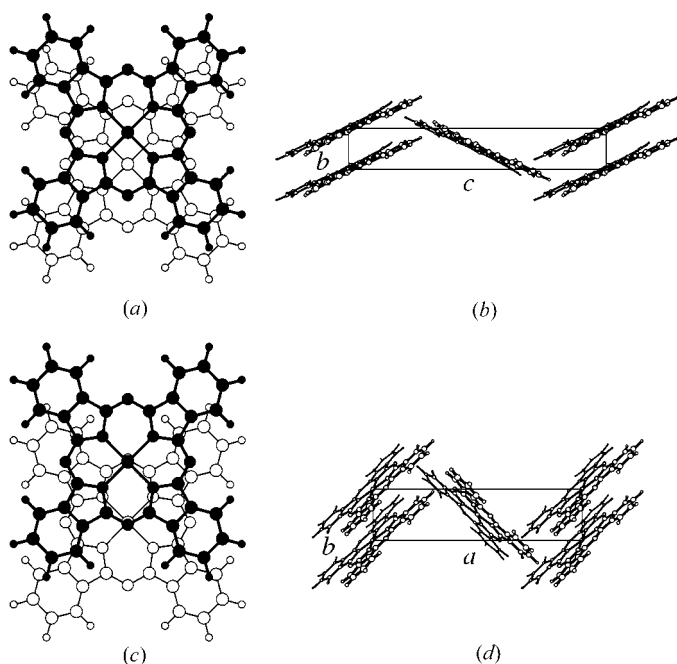
In the case of CuPc, only the β-modification was fully analyzed by X-ray diffraction (Brown, 1968*a*). A frequently cited report on α-CuPc is that of Ashida *et al.* (1966), who studied the crystal structure of CuPc grown epitaxially on mica and determined its lattice constants by electron diffraction on the assumption that the CuPc was isostructural with α-PtPc. Ashida also studied the epitaxy of CuPc on alkali-halide substrates (Ashida, 1966*a*) and found that α-CuPc crystals

took better epitaxic orientation on KCl than on KBr. Although he did not discuss the interface structures in detail, Ashida attributed this result to the difference of the misfits at the interfaces.

In order to clarify the effect of the misfits, we began to reinvestigate the epitaxy of CuPc on alkali-halide surfaces. In the course of our investigation we found the crystal structure proposed by Ashida *et al.* (1966) to be incorrect. In this paper we report the detailed analysis for the crystal structure of CuPc grown on KCl and show that the structure is different from the α-modifications of H_2Pc (Janczak & Kubiak, 1992) and platinum phthalocyanine (PtPc) (Brown, 1968*b*); the structure we find has a parallel molecular arrangement rather than a herringbone-type molecular arrangement. In addition, we show by carrying out Rietveld analysis that the structure we have analyzed is actually so-called α-CuPc. We therefore conclude that α-CuPc is isostructural with neither α-H_2Pc nor α-PtPc.

This is not the first report that proposes a parallel molecular arrangement of α-phthalocyanines. Honigmann *et al.* (1965) had already proposed a parallel molecular arrangement for α-CuPc (or αI-CuPc according to his nomenclature) and Ballirano *et al.* (1998) recently reported the structure of α-CoPc which is quite similar to Honigmann's model. However, the structure we have determined is different from these structures in the molecular stacking mode within a molecular column.

Since the nomenclature of the polymorphs of phthalocyanines is very misleading, we classify the crystal structures of planar phthalocyanines forming molecular columns into four types in terms of molecular stacking mode within a molecular column.

2. Experimental

A single crystal of KCl was placed on a sample holder in a vacuum chamber. After the chamber was evacuated to 1×10^{-4} Pa, the crystal was cleaved and heated to 493 K. CuPc purchased from Aldrich Chemical Co. was deposited on this substrate. The thickness of each CuPc crystal grown on the substrate was ~ 3000 Å. For structure analysis CuPc crystals as thin as 50 Å were prepared by deposition at room temperature. The CuPc deposited on KCl was reinforced by an evaporated carbon film. After the KCl substrate was dissolved in water, the carbon-coated CuPc was fixed on an electron microscope copper grid covered with a microgrid. Gold had already been deposited on this microgrid, which we used as a standard sample when measuring spacings of lattice planes. The accuracy of the lattice spacings was 0.3%. The sample was observed by a transmission electron microscope (TEM, JEOL JEM-1200EXII). In order to vary the incident electron beam direction towards the sample during the transmission electron diffraction (TED) experiment, a sample holder that can rotate and tilt a sample was used: the maximum tilt angle was 60°. Electron diffraction patterns were recorded on imaging plates (Fuji DL UR-III) and were read out by an imaging plate reader (Rigaku R-AXIS DS-II) with a resolution of 50 μm.

In order to compare the crystal structure of CuPc grown on KCl with that of α-CuPc, we prepared α-CuPc by acid treatment of β-CuPc and carried out a Rietveld analysis. α-CuPc was obtained by dissolving CuPc in concentrated sulfuric acid (97%), followed by reprecipitation by diluting the solution with water. After the precipitate was filtered, washed with water and dried, it was ground and packed into a glass capillary of 0.3 mm diameter. A powder X-ray diffraction profile of the sample was obtained by the Debye–Scherrer method using a Rigaku RU-3V diffractometer operated at 40 kV and 60 mA. X-ray radiation generated from a rotating-anode tube (Cu target) was monochromated with graphite in order to obtain incident Cu $K\alpha_{1,2}$ radiation. The sample attached to a Debye–Scherrer camera was set in a vacuum chamber together with an imaging plate and the chamber was evacuated by a rotary pump during exposure. A diffraction pattern recorded on the imaging plate was read out by the imaging plate reader and was converted to an intensity profile data [step size = 0.049716 (3)°]. The step size had been measured in advance using powder X-ray data of Si. Experimental details are given in Table 1.

3. Results

3.1. Electron diffraction

Fig. 2(*a*) shows a TED image of a single crystal of CuPc grown on KCl. In this experiment the incident electron beam was perpendicular to the surface of the film specimen; the sample was not tilted in the TEM. By tilting the specimen
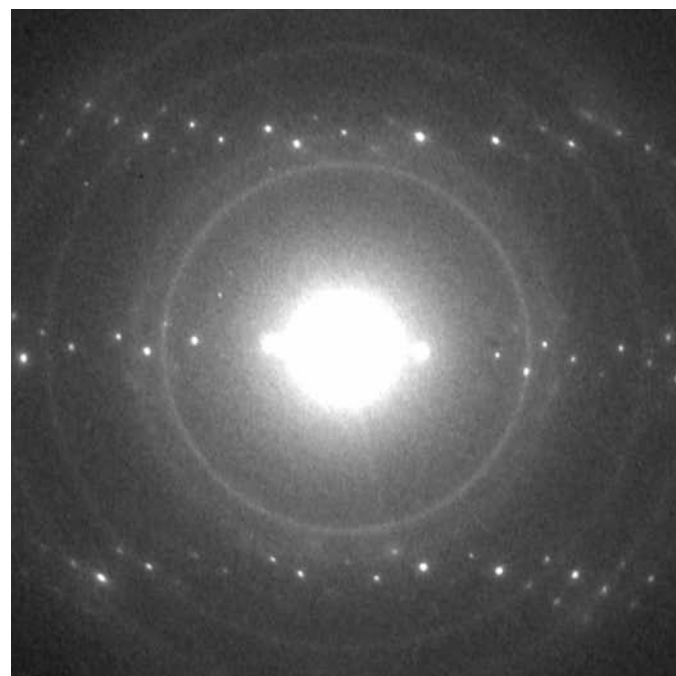

Figure 1
Typical crystal structures of planar phthalocyanines: (*a*) and (*b*) the α-modification; (*c*) and (*d*) the β-modification. (*a*) and (*c*) represent the overlapping of neighbouring molecules within a molecular column. Both structures have herringbone-type molecular packings.

Table 1
Experimental table.

Crystal data

Chemical formula	$C_{32}H_{16}CuN_8$
M_r	576.07
Cell setting, space group	Triclinic, $P\bar{1}$
a, b, c (Å)	12.886 (2), 3.769 (3), 12.061 (3)
α, β, γ (°)	96.22 (7), 90.62 (4), 90.32 (8)
V (Å³)	582.3 (5)
Z	1
D_x (Mg m⁻³)	1.643
Radiation type	Cu $K\alpha_1$, Cu $K\alpha_2$
μ (mm⁻¹)	1.67
Temperature (K)	295
Specimen form, colour	Cylinder, dark blue
Specimen size (mm)	$5 \times 0.3 \times 0.3$

Data collection

Diffractometer	Rigaku RU-3V
Data collection method	Specimen mounting: quartz capillary; mode: transmission; scan method: fixed
Absorption correction	None
2θ (°)	$2\theta_{min} = 6.016$, $2\theta_{max} = 59.957$, increment = 0.050

Refinement

Refinement on	I_{net}
R factors and goodness of fit	$R_p = 0.024$, $R_{wp} = 0.033$, $R_{exp} = 0.016$, $S = 2.05$
Wavelength of incident radiation (Å)	1.54056–1.54439
Excluded region(s)	60–95.8°; too small peak intensities
Profile function	Pseudo-Voigt
No. of parameters	83
H-atom treatment	H-atom parameters not defined
Weighting scheme	$1/y_i$
$(\Delta/\sigma)_{max}$	<0.0001

Computer programs: *R-AXIS* (Rigaku Corporation, 1996), *RIETAN*2000 (Izumi, 2002*b*).

tion, we noticed several problems in their analysis. First, if their indexing is correct, the space group must be $C2/n$ or $B2_1/a$ rather than $C2/c$. The indices they assigned were all odd or all even, which means that centred metals of CuPc form a lattice similar to a face-centred cubic lattice (Brown, 1968*b*). This pattern is not consistent with the space group $C2/c$; in the case of $C2/c$, molecules within a unit cell must reside at (0, 0, 0), (1/2, 1/2, 0), (1/2, 1/2, 1/2) and (0, 0, 1/2). $C2/n$ and $B2_1/a$, which were reported for other phthalocyanines such as PtPc (Brown, 1968*b*), are consistent with the indexing of Ashida *et al.* (1966). Hence, we must have at least modified the space group or the indexing. Secondly, Ashida *et al.* (1966)

(*a*)

(*b*)

Figure 2
Transmission electron diffraction (TED) images of a single crystal of CuPc. (*a*) The incident electron beam was perpendicular to the specimen film: the specimen was not tilted. (*b*) By tilting the specimen through 32° around the horizontal axis, a clear net pattern was observed.
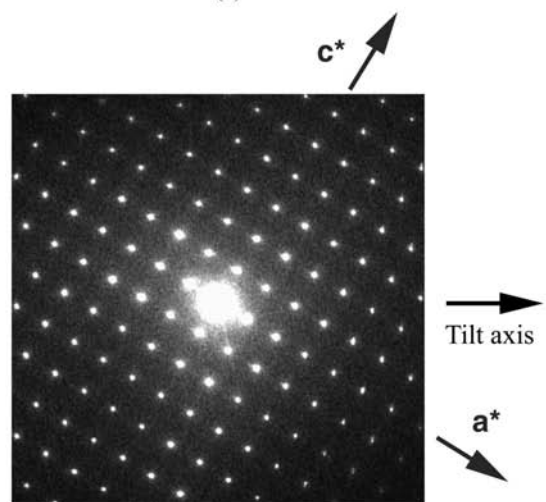
around the horizontal axis of Fig. 2(*a*) by 32°, we obtained the clear net pattern shown in Fig. 2(*b*). These two diffraction patterns seem to be the same as those reported previously (Ashida *et al.*, 1966; Ashida, 1966*a*). We compared our diffraction patterns with the original photographs taken by Ashida, which are kept in Kyoto University as a part of his doctoral thesis (Ashida 1966*b*). We confirmed that our patterns are exactly the same as his patterns. The difference between our results and his is the epitaxic orientation of CuPc. In our experiment, the horizontal axis of Fig. 2(*a*) was found to be parallel to ⟨100⟩ of KCl, whereas he reported that it was parallel to ⟨110⟩ of KCl (Ashida, 1966*a*). We made several samples by changing the substrate temperature, but we could not reproduce his result. This discrepancy will be discussed elsewhere.

Concerning the crystal structure, Ashida *et al.* (1966) reported the lattice constants of CuPc grown on mica and KCl ($C2/c$, $Z = 4$, $a = 25.92$, $b = 3.79$, $c = 23.92$ Å and $\beta = 90.4°$), and indexed the same diffraction pattern as Fig. 2(*a*) by using these lattice constants. In order to confirm their indexing, we calculated the diffraction pattern on a computer. However, we failed to reproduce the pattern. In the course of our calcula-

concluded that the $(31\bar{3})$ plane of CuPc was parallel to the substrate surfaces. We found that the $(21\bar{4})$ plane rather than the $(31\bar{3})$ plane should have been parallel to the substrate surface if either the space group or the indices they assigned is correct. Lastly, even if we take these modifications into account, we fail to reproduce the diffraction pattern of Fig.

(a)

(b)

(c)
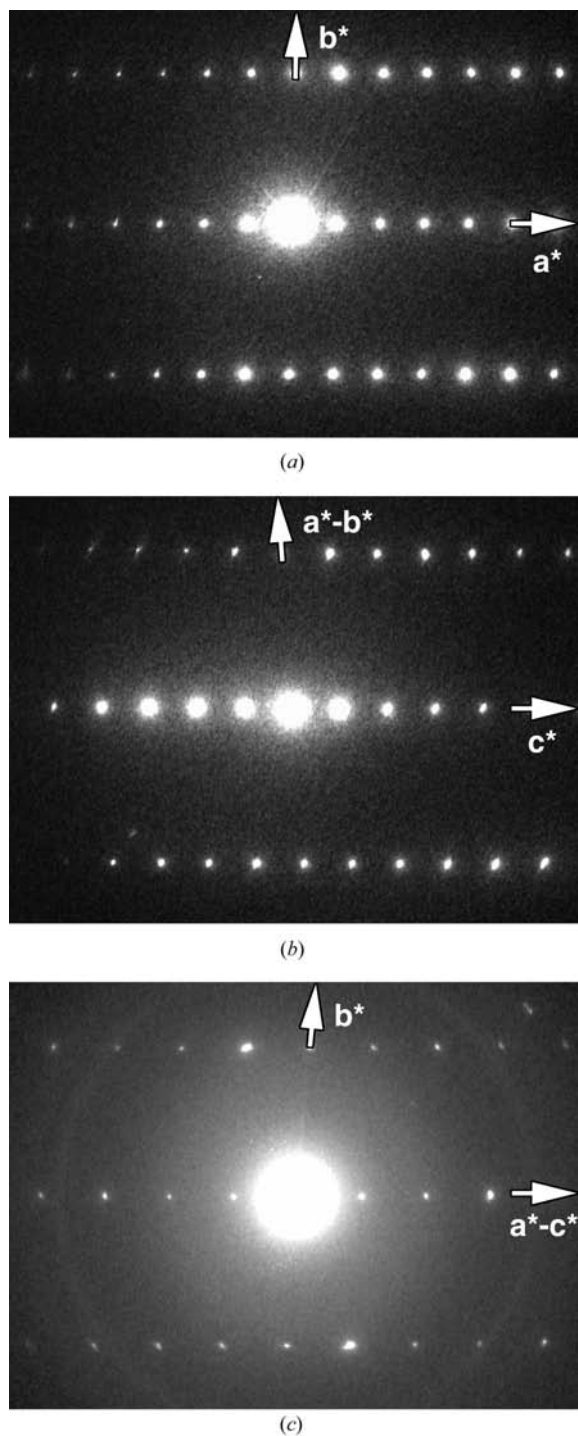
Figure 3
TED images of CuPc with different incident beam directions. Incident beams of *(a)*–*(c)* are parallel to $[001]_{CuPc}$, $[110]_{CuPc}$ and $[101]_{CuPc}$, respectively.

2(*a*). We tried to modify the lattice parameters, but we could not obtain any satisfactory result. We therefore conclude that the model proposed by Ashida *et al.* (1966) is not correct.

In order to determine the correct lattice constants, we first examined the patterns shown in Figs. 2(*a*) and (*b*). Since these figures correspond to two sections of the reciprocal lattice, we can estimate the lattice constants. We adopted the same $\mathbf{a}^*$ and $\mathbf{c}^*$ values as Ashida *et al.* (1966) in Fig. 2(*b*) and estimated the lattice constants to be $a = 25.84$, $b = 3.80$, $c = 23.92$ Å, $\alpha = 94.8$, $\beta = 90.1$ and $\gamma = 91.3°$. As these values indicate, the crystal system is triclinic rather than monoclinic; we tried other candidates for $\mathbf{b}^*$, but we could not find any appropriate monoclinic unit cell. Using these values, we calculated several sets of sample rotation and tilt angles for clear net patterns such as the $\mathbf{a}^*\mathbf{b}^*$ plane. By rotating and tilting the sample through the calculated values, we obtained various diffraction patterns (Fig. 3). Fig. 3(*c*) shows clearly that the crystal system is triclinic: if it were monoclinic, $\mathbf{a}^* - \mathbf{c}^*$ would be perpendicular to $\mathbf{b}^*$. Moreover, these patterns were all indexed to $2m\ k\ 2n$ (m, n: integers); namely, $2m + 1\ k\ 2n$ or $2m\ k\ 2n + 1$ spots could not be observed in any diffraction pattern. Consequently, we should have taken both a and c to be half the values described above. According to this modification, the plane of CuPc parallel to the substrate surface should be the $(11\bar{2})$ plane rather than the $(21\bar{4})$ plane.

By analysing these diffraction patterns in detail, we finally determined the lattice constants to be $a = 12.91$ (4), $b = 3.81$ (1), $c = 12.00$ (5) Å, $\alpha = 95.6$ (3), $\beta = 90.1$ (1) and $\gamma = 91.0$ (2)°. Since the unit cell contains only one molecule ($Z = 1$), the crystal does not have a herringbone-type molecular arrangement; it is not isostructural with the α- and β-modifications shown in Fig. 1. Considering the D_{4h} symmetry of an isolated CuPc molecule, we could assume the space group to be $P\bar{1}$ rather than $P1$.

3.2. Molecular packing analysis

The lattice constants determined indicate that all CuPc molecules have the same orientation in the crystal. This type of molecular packing of CuPc has been observed directly by high-resolution electron microscopy (Ueda *et al.*, 1994) and scanning tunnelling microscopy (Hiesgen *et al.*, 2000), but its detailed structure has not been clarified.

In order to obtain plausible models of the molecular packing, we calculated molecular packing energy using a local program, varying the molecular orientation in a unit cell. In the calculation, the lattice parameters and the molecular shape were fixed and the internal coordinates of atoms in the molecule were taken from those reported (Schaffer *et al.*, 1973). Molecular packing energy was calculated as the sum of the interaction energy between one molecule and 44 (= $3 \times 5 \times 3 - 1$) neighbouring molecules. The Buckingham-type potential function with the Universal Force Field parameters (Rappé *et al.*, 1992) was used for the calculation of the van der Waals interaction energy, and electrostatic interactions between molecules were also taken into account.

Table 2
$|F(hkl)|^2$ (Å^2) calculated for Model I and Model II.

hkl	Model I	Model II
001	307	208
002	75	269
10$\bar{2}$	228	423
10$\bar{1}$	6	27
100	258	318
101	3	11
102	349	87
20$\bar{2}$	9	4
20$\bar{1}$	466	230
200	220	125
201	104	366
202	31	30

For the molecular packing with minimum energy, we obtained two models (Model I and Model II in Fig. 4). The atomic coordinates of Models I and II have been deposited.[1] These models differ not only in molecular orientation but also in the molecular stacking direction projected onto the molecular plane within a molecular column; we hereafter call the direction *the molecular offset direction*. Model I has the same molecular offset direction as those of the α- and β-modifications, whereas Model II has a different direction from Model I by ∼ 45°. Model I has basically the same molecular packing as the structures proposed for α-CuPc (or αI-CuPc according to Honigmann's nomenclature; Honigmann *et al.*, 1965) and α-CoPc (Ballirano *et al.*, 1998). Besides these models, Murata *et al.* (1976) proposed a molecular orientation rotated from that of Models I and II, based on a high-resolution molecular image of CuPc grown on KCl. We could not obtain any model similar to their model by our calculation. The periodicities of the high-resolution image along the *a* and *c* axes are 12.96 and 11.96 Å, respectively, which are practically the same as those of our data, $d(100) = 12.91$ and $d(001) = 11.94$ Å. Hence, the crystal they reported would be the same as ours. Since the quality of the molecular image is unfortunately not so high, the validity of their model is open to question.

The result of our calculation is that Model II is more stable by 13 kJ mol^{-1} than Model I. In the next section we decide which model corresponds to the real structure by analysing the diffraction intensities of CuPc.

3.3. Intensity analysis of TED pattern

Since the molecular orientation of Model I projected along the *b* axis is different from that of Model II (Fig. 4), it is sufficient to examine the diffraction intensities of *h0l* reflections to decide between the two models. When a specimen is so thin that the kinematical theory of electron diffraction is applicable, the intensity of the *hkl* reflection is directly proportional to $|F(hkl)|^2$, where $F(hkl)$ is the structure factor. Table 2 lists several values of $|F(hkl)|^2$ calculated for the two models. As can be seen from Table 2, $|F(hkl)|^2$ has two characteristics. One is that the *h0h* and *h0h̄* reflections have very small intensities in both cases. The other is that when $|F(h0l)|^2$ ($h \neq l$) is greater than $|F(l0h)|^2$ in one model, the former is always smaller than the latter in the other model. In particular, $|F(102)|^2$ is three times greater than $|F(201)|^2$ in Model I, whereas the former is one fourth of the latter in Model II, and hence these reflections can be used to decide between the two models.

In order to check the dynamical effect on the diffraction intensities, we also calculated the thickness dependence of the intensities. The calculation was carried out with commercial software, *MacTempas* (Total Resolution, 2001). Fig. 5 shows the thickness dependence of the intensities of the 102, 201, 20$\bar{1}$ and 10$\bar{2}$ reflections of the two models. When the thickness is ∼100 Å, the magnitude relation between the intensities differs from that of the thinner conditions owing to the dynamical effect. On the other hand, if the thickness is below 60 Å, the dynamical effect is found to be negligible. In the case of Fig. 2(*b*), we could not apply the kinematical theory since the thickness of the crystal was estimated to be ∼3000 Å by atomic force microscopy; no distinct differences were observed between the intensities of the spots.

Fig. 6(*a*) shows a TED image of a thinner sample, 50 Å thick, prepared by deposition at room temperature. The sample was tilted by 32° around the horizontal axis in Fig. 6, which was parallel to ⟨100⟩ of KCl. CuPc crystals in this sample were found to have the same epitaxic orientation and lattice constants as those of the thicker sample. Fig. 6(*a*) shows two **a*****c*** net patterns with different orientations. Fig. 6(*b*) represents schematically one of the net patterns, in which the intensity of each diffraction spot is represented by its area. The 101, 202, 10$\bar{1}$ and 20$\bar{2}$ spots have weaker intensities (see Table 3). The intensity of the 102 spot is very weak and the 201 spot, on the other hand, is very strong. In addition to this, the intensities of the 002, 100 and 10$\bar{2}$ spots are stronger than those of the 200, 001 and 20$\bar{1}$ spots, respectively, which is consistent with the calculation for Model II. We therefore conclude that Model II corresponds to the real structure.

3.4. Comparison with reported structures

We have determined the molecular packing of CuPc crystals grown on KCl and found that the structure is not isostructural with the α- and β-modifications shown in Fig. 1. Since various polymorphs of CuPc have been reported so far, the structure we have determined has the possibility of being one of those polymorphs. In order to clarify this situation, we calculated a powder X-ray diffraction profile expected for the new crystal structure (Model II). For comparison, we also calculated it for Model I. In this calculation, each reflection was assumed to have a Lorentzian distribution with a full width at half maximum of 0.5°. A wavelength of 1.5418 Å (Cu Kα) was used.

Fig. 7 shows the result of the calculation. Surprisingly, the two models gave quite similar patterns and these are also similar to those reported for α-CuPc (Wiswall, 1949; Pfeiffer, 1962; Knudsen & Rolskov, 1964; Assour, 1965; Honigmann *et al.*, 1965). As we mentioned earlier, Honigmann *et al.* (1965)

and Ballirano *et al.* (1998) proposed models similar to Model I for α-CuPc and α-CoPc, respectively. Our calculation suggests two possibilities. One is that the crystal structure we have found is a new polymorph of CuPc that gives a similar powder pattern to that of α-CuPc. The other is that the structure is really α-CuPc and that Honigmann's model is not correct.

3.5. Rietveld analysis for α-CuPc

We carried out a Rietveld analysis for α-CuPc with the program *RIETAN*2000 (Izumi & Ikeda, 2000). In our analysis, the pseudo-Voigt function of Thompson *et al.* (1987) was used to describe each peak, and peaks were made asymmetric using the method of Finger *et al.* (1994). Among the ten parameters U, V, W, P, X, X_e, Y, Y_e, r_s and r_d, which describe the peak function, U, P, X_e and Y_e were fixed at 0 for the sake of simplicity. In addition to this, r_s and r_d were also fixed at 0.0075. The preferred-orientation parameter, r, was fixed at 0 and the overall isotropic atomic displacement parameter was

fixed at 2.5 Å^2. Experimental data in the 2θ range 6–60° were used for the refinement.

We tried Model I (Refinement I) and Model II (Refinement II) as the initial structures. All H atoms were excluded from the models. We imposed 68 nonlinear restraints on bond distances and angles during the refinements, which were expressed by the following penalty function (Izumi, 2002*a*)

$$\chi_r^2 = t \sum_j (1/l_j^{\text{cal}}) \big[\min\{0, \Delta l_j - |l_j^{\text{cal}} - l_j^{\text{exp}}|\} \big]^2, \quad (1)$$

where t is the global weight factor for the restraints, l_j^{cal} the calculated value for the corresponding jth restraint, l_j^{exp}, the expected value, and Δl_j an allowance. We allowed deviations of $\Delta l_j = 0.01$ Å and 0.9° from the initial bond lengths and angles, respectively, without penalty on the χ^2 function that was to be minimized. These allowances were determined from the molecular structure of β-CuPc (Brown, 1968*a*). t was set to be 250 000. The space group was assumed to be $P\bar{1}$. It should be noted that the molecular packing of each model was basically unchanged during the refinements.

Fig. 8 shows the final fits between experimental and calculated profiles for the two refinements, and refinement details are presented in Table 3. It seems that both refinements gave reasonable agreement between the calculated and observed intensities. R factors of Refinement I were $R_{\text{wp}} = 0.045$, $R_p = 0.035$ and $R_F = 0.011$. On the other hand, Refinement II gave $R_{\text{wp}} = 0.033$, $R_p = 0.024$ and $R_F = 0.007$. As the R factors indicate, Refinement II gave better agreement between the calculated and observed intensities. In particular, the observed peaks in the 2θ range 30–60° were better reproduced in Refinement II. For example, the peaks at 32 and 56° in the experimental data were not reproduced in Refinement I, whereas Refinement II gave peaks at these angles.

In order to check whether the model obtained by Refinement II is significantly better or not, we carried out a significance test using Prince's method (Prince, 1982): this method examines the correlation between the differences in the predictions of the models and the corresponding differences between the observed data and the arithmetic means of the predictions. The 99.9% confidence interval for the slope of the regression line was calculated to be −0.41 (10), where the slope would be expected to be positive if the model obtained by Refine-
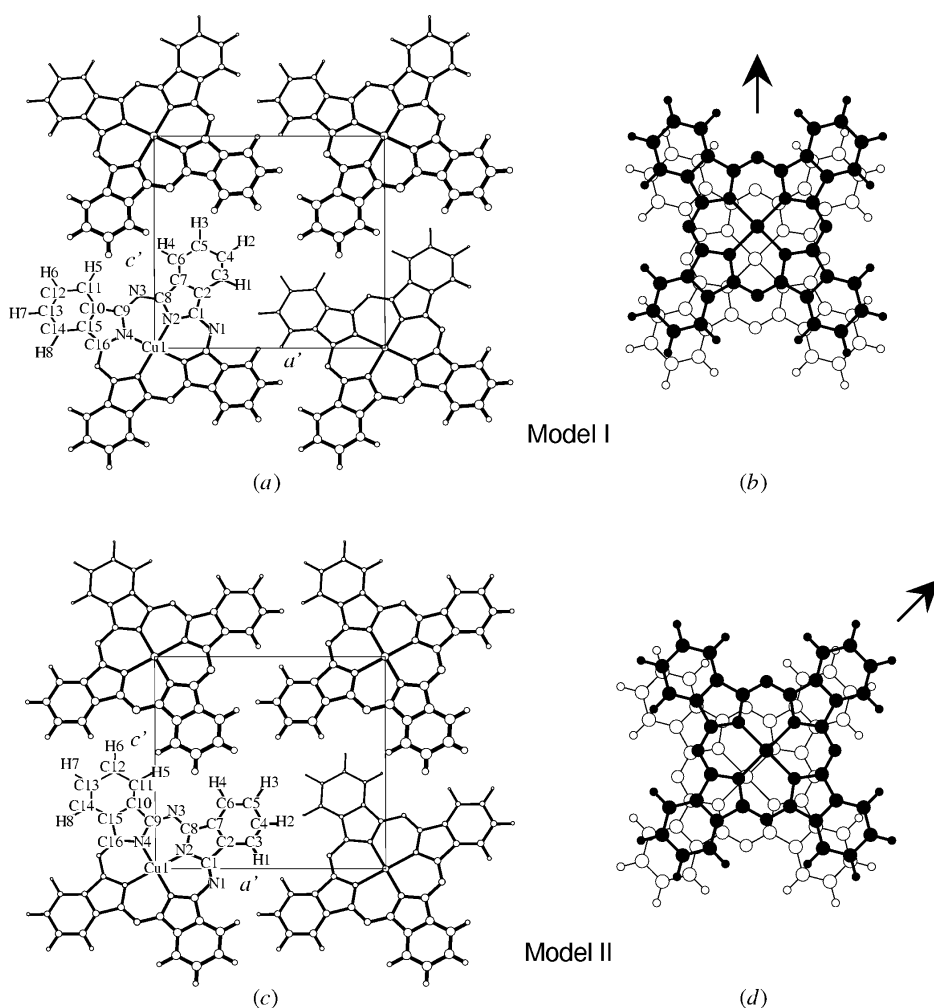
Figure 4
Two models for the CuPc crystal obtained by the calculation of molecular packing energy: (*a*) and (*b*) for Model I and (*c*) and (*d*) for Model II. (*a*) and (*c*) show the projections along the *b* axis. (*b*) and (*d*) represent the overlapping of neighbouring molecules within a molecular column. The molecules stack with an offset, the direction of which is represented by the arrow in each figure.

Table 3
Refinement details.

	Refinement I	Refinement II
$2\theta_{\min}$ (°)	6.016	6.016
$2\theta_{\max}$ (°)	59.957	59.957
Step size (°)	0.050	0.050
Radiation type	Cu $K\alpha_{1,2}$	Cu $K\alpha_{1,2}$
Number of profile points	1086	1086
Number of bond-length restraints	26	26
Number of bond-angle restraints	42	42
Number of parameters	83	83
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
a (Å)	12.898 (3)	12.886 (2)
b (Å)	3.771 (3)	3.769 (3)
c (Å)	12.079 (4)	12.061 (3)
α (°)	96.17 (8)	96.22 (7)
β (°)	89.51 (6)	90.62 (4)
γ (°)	90.6 (1)	90.32 (8)
V (Å³)	584.0 (6)	582.3 (5)
R_{wp}	0.045	0.033
R_p	0.035	0.024
R_F	0.011	0.007
Reduced χ^2	7.89	4.21
Profile contribution to reduced χ^2	7.40	3.93
Restraint contribution to χ^2	525	292
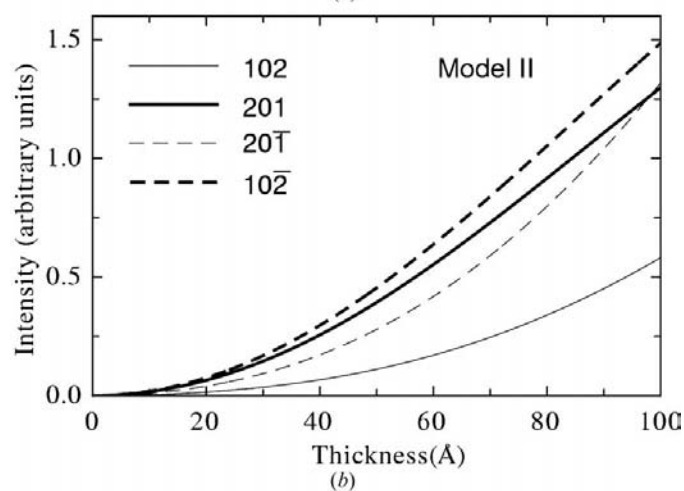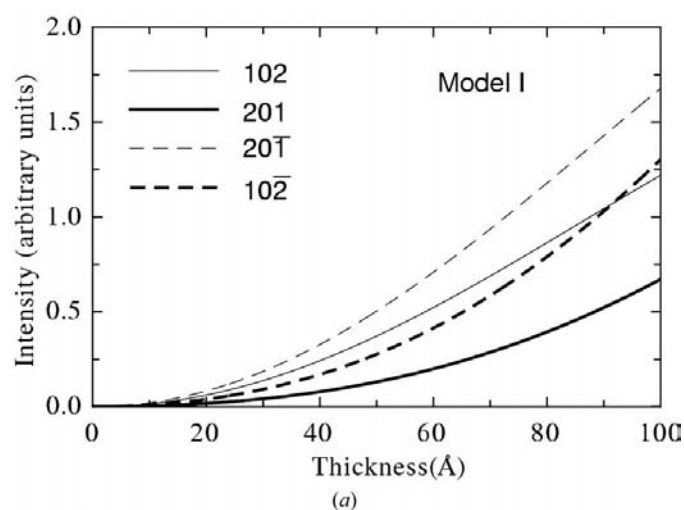
Figure 5
Thickness dependences of the TED intensities of the 102, 201, 20$\bar{1}$ and 10$\bar{2}$ spots calculated for (a) Model I and (b) Model II.

ment I was better. Hence, the hypothesis that the two structures give equally good fits to the experimental data was rejected at the 0.1% confidence level.

Fig. 9 shows top and side views of the molecules obtained from the refinements. As can be seen in the side views, the molecular shape obtained from Refinement I (Fig. 9a) is unnaturally bent, whereas the bend in the case of Refinement II (Fig. 9b) is much less. The contribution of nonlinear restraints on χ^2 also indicates a larger deviation of the molecular shape from the initial molecular shape in Refinement I: the contributions in the cases of Refinements I and II were 525 and 292, respectively.

We conclude from these results that Model II is more likely to be the true crystal structure of α-CuPc; the molecular packing of α-CuPc is the same as that of CuPc grown on KCl.
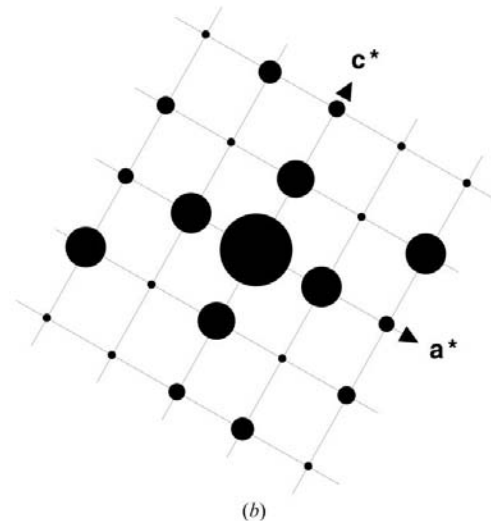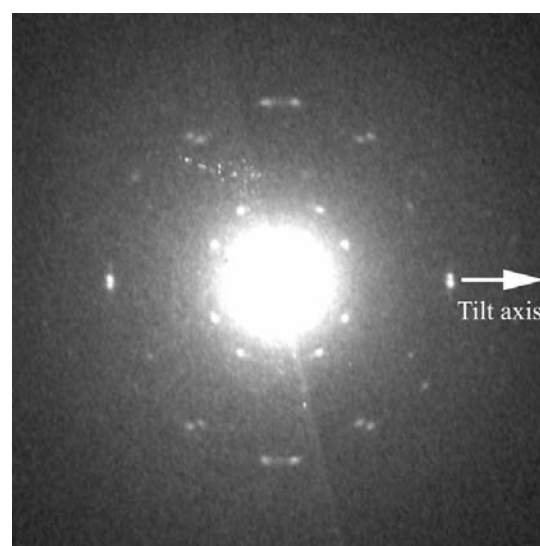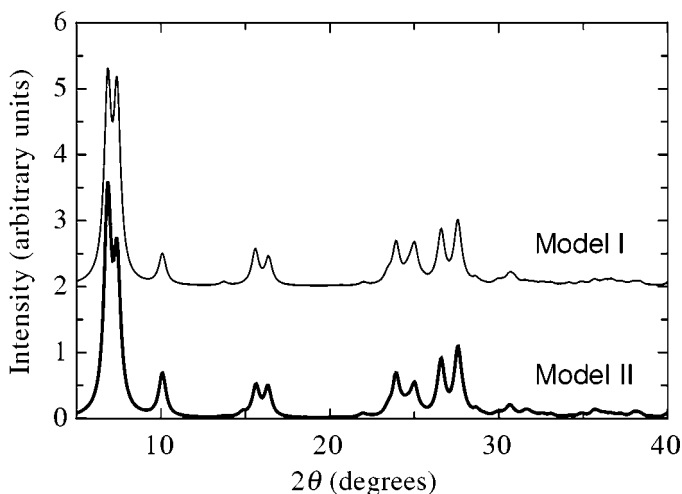

Figure 6
(a) A TED image of a very thin CuPc film (50 Å). The specimen was tilted by 32° around the horizontal axis. This image consists of two net patterns with different orientations. One of the net patterns is schematically represented in (b). The intensity of each diffraction spot is represented by its area.

The refined lattice parameters obtained from Refinement II are $a = 12.886$ (2), $b = 3.769$ (3), $c = 12.061$ (3) Å, $\alpha = 96.22$ (7), $\beta = 90.62$ (4) and $\gamma = 90.32$ (8)°. Taking into account the fact that the standard deviations of the Rietveld refinements are known to be optimistic (Bérar & Lelann, 1991), these lattice parameters are practically the same as those determined by TED: $a = 12.91$ (4), $b = 3.81$ (1), $c = 12.00$ (5) Å, $\alpha = 95.6$ (3), $\beta = 90.1$ (1) and $\gamma = 91.0$ (2)°. We therefore conclude that the CuPc crystals grown on KCl were actually α-CuPc and that the model of α-CuPc proposed by Honigmann is not correct.

Moxon et al. (1981) reported the lattice constants of α-CuPc determined by a powder X-ray measurement to be: $a = 25.9$ (1), $b = 3.80$ (1), $c = 24.7$ (1) Å, $\alpha = 90.00$ (2), $\beta = 90.09$ (2) and $\gamma = 95.60$ (2)°. Their values for a and c are twice as large as ours and their angles are not consistent with our result, even if we change the assignment of the axes. Since they did not show their powder X-ray diffraction profile, we cannot estimate the quality of their data. The discrepancy between their data and our data remains unknown.

Fig. 10(a) represents the a axis projection of α-CuPc. This molecular arrangement is the same as the high-resolution molecular image reported by Ueda et al. (1994). They reported that the distance between molecular columns was 12 Å and that molecular stripes made an angle of 63° with the column axis. These values coincide with those of α-CuPc, as shown in Fig. 10(a). Although Ueda et al. considered their material to be a polymorph different from α-CuPc, it was actually α-CuPc as our investigation has revealed.

Fig. 10(b) is a schematic representation of a molecular column of α-CuPc. The distance between neighbouring molecular planes is 3.42 Å and the direction normal to the molecular planes makes an angle of 24.9° with the column direction. Molecules stack along the b axis with an offset of 1.58 Å. In the case of α-PtPc, the corresponding values are 3.45 Å, 25.5° and 1.64 Å, respectively (Brown, 1968b). Although these values are quite similar to those of α-CuPc,
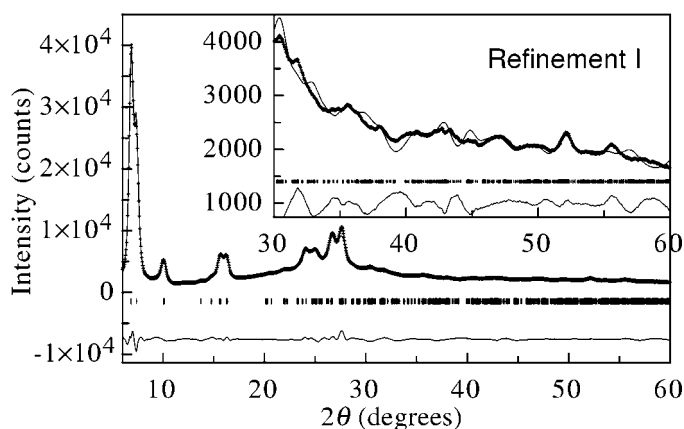
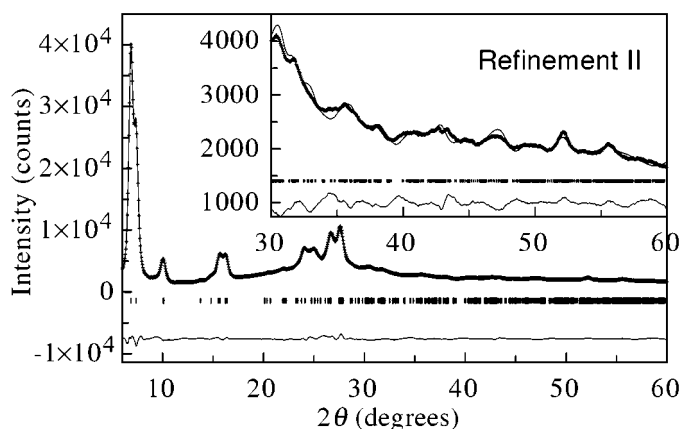these two structures have different molecular offset directions and are not isostructural.

4. Discussion

As had already been noticed by Honigmann et al. (1965), α-CuPc (or αI-CuPc according to Honigmann's nomenclature) is not isostructural with α-PtPc and it is rather γ-CuPc (or αII-CuPc according to Honigmann's nomenclature; Eastes, 1956) that is isostructural with α-PtPc. However, researchers have been using the terms α-CuPc, α-PtPc and α-modifications for many years and it seems that these terms have brought some confusion and misunderstanding about the crystal structures of phthalocyanines. This confusion is also pointed out in the recent book written by Bernstein (2002).

We therefore propose a classification of the crystal structures of planar phthalocyanines forming columnar structures in terms of the molecular stacking mode within the molecular column and give a name for each stacking type: the classification and naming would be useful for understanding the crystalline phases of the phthalocyanines.

Figure 7
Powder X-ray diffraction profiles calculated for Model I (thin line) and Model II (thick line).

Figure 8
The final fits between experimental and calculated diffraction profiles for (a) Refinement I and (b) Refinement II.

Many crystal structures of planar phthalocyanines forming columnar structures have been reported. As is well known, these structures can roughly be classified into two groups depending on the length of the shortest crystal axis, *i.e.* the direction that corresponds to the stacking direction of phthalocyanine molecules within the molecular column. One group has a length of ~ 3.8 Å and the other of ~ 4.8 Å. For example, α-CuPc, α-PtPc and α-H$_2$Pc belong to the former group and the β-modifications shown in Fig. 1(*b*) to the latter group. Also, χ-H$_2$Pc, investigated recently (Oka & Okada, 1993; Hammond *et al.*, 1996; Zugenmaier *et al.*, 1997; Janczak, 2000), can be classified in the latter group. This criterion may be applicable not only to the planar phthalocyanines, but also to planar aromatic hydrocarbon crystals. Desiraju and co-workers classified them into four types: HB-, SHB-, β- and γ-types (Desiraju & Gavezzotti, 1989; Desiraju, 1989), among which the β- and γ-types have columnar structures and correspond to the α- and β- modifications of the phthalocyanines. These authors showed that there is quite a distinction between β- and γ-types; the length of the shortest axis of the β-type is less than 4.0 Å and that of the γ-type is larger than 4.4 Å.

However, it is now obvious that this criterion is not sufficient for the identification of the polymorphs of the phthalocyanines. Another important point that characterizes the polymorphs of the phthalocyanines is *the molecular offset direction*. The α- and β-modifications shown in Fig. 1 have the same molecular offset direction. On the other hand, the molecular offset direction of α-CuPc is different by $\sim 45^\circ$ from

that of these modifications. χ-H$_2$Pc also has the same molecular offset direction as α-CuPc (Oka & Okada, 1993; Hammond *et al.*, 1996; Zugenmaier *et al.*, 1997; Janczak, 2000).

From these two points, we classify the stacking modes of phthalocyanine molecules within a molecular column into four types: $\alpha(\times)$-, $\alpha(+)$-, $\beta(\times)$- and $\beta(+)$-types (Fig. 11). Typical examples of the $\alpha(\times)$-type are α-PtPc (Brown, 1968*b*) and α-H$_2$Pc (Janczak & Kubiak, 1992). The lengths of the shortest axes of these crystal structures are ~ 3.8 Å and their molecular offset directions are identical. Since the phthalocyanine molecules have a cross shape, their molecular stackings within a molecular column look like '$\times\times\times\times\times$...' which is the reason why we adopt $\times$ in our nomenclature. On the other hand, the molecular offset direction of α-CuPc is different by $\sim 45^\circ$ from those of α-H$_2$Pc and α-PtPc, although the shortest axes are almost the same as in α-PtPc and α-H$_2$Pc. Since the molecular stacking of α-CuPc within a molecular column looks like '+++++...' we named this stacking the $\alpha(+)$-type. As the name indicates the $\beta(\times)$-type is that of the β-modifications and a typical example of the $\beta(+)$-type is χ-H$_2$Pc (Oka & Okada, 1993; Hammond *et al.*, 1996; Zugenmaier *et al.*, 1997; Janczak, 2000).

According to this classification, crystal structures of various planar phthalocyanines can be classified into four groups.

In the case of the $\alpha(+)$-group, α-CuPc and perchloro-copper phthalocyanine (Cl$_{16}$CuPc; Uyeda *et al.*, 1972) surely belong to this group. Since Cl$_{16}$CuPc crystallizes into a monoclinic structure ($Z = 2$, $a = 19.62$, $b = 26.04$, $c = 3.76$ Å and $\beta = 116.5^\circ$; Uyeda *et al.*, 1972), it is not completely isostructural with α-CuPc. However, all Cl$_{16}$CuPc molecules within a crystal have an identical orientation, as in α-CuPc; the two structures are closely related to each other. Besides these crystal structures, monochloro-copper phthalocyanine (ClCuPc) was reported to be isostructural with α-CuPc (Honigmann *et al.*, 1965), although its structure has not been fully analyzed. α-Cobalt phthalocyanine (CoPc; Ballirano *et al.*, 1998) may also belong to this group; we will discuss the crystal structure of α-CoPc later. The $\alpha(+)$-group hence contains two types of crystal structures that resemble each other. It should be noted that only the crystal structures of this group do not have a herringbone-type molecular arrangement.

The $\beta(\times)$-group contains only one polymorph, *i.e.* the β-modification shown in Fig. 1(*b*). Concerning the $\beta(+)$-group, two types of crystal structures have been reported thus far for χ-H$_2$Pc (Oka & Okada, 1993; Hammond *et al.*, 1996; Zugenmaier *et al.*, 1997; Janczak, 2000). We do not
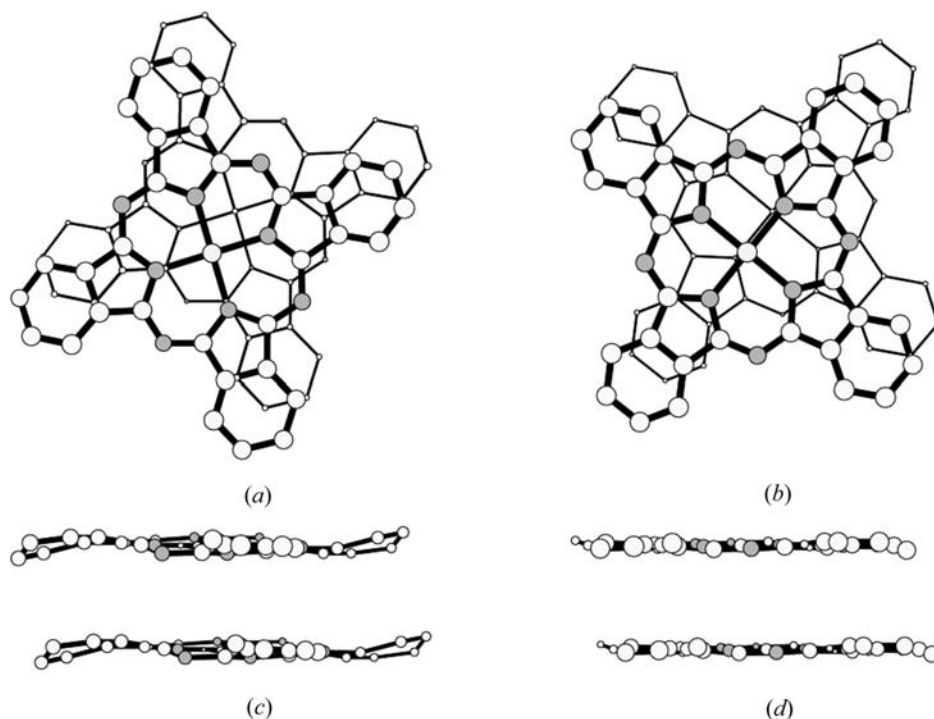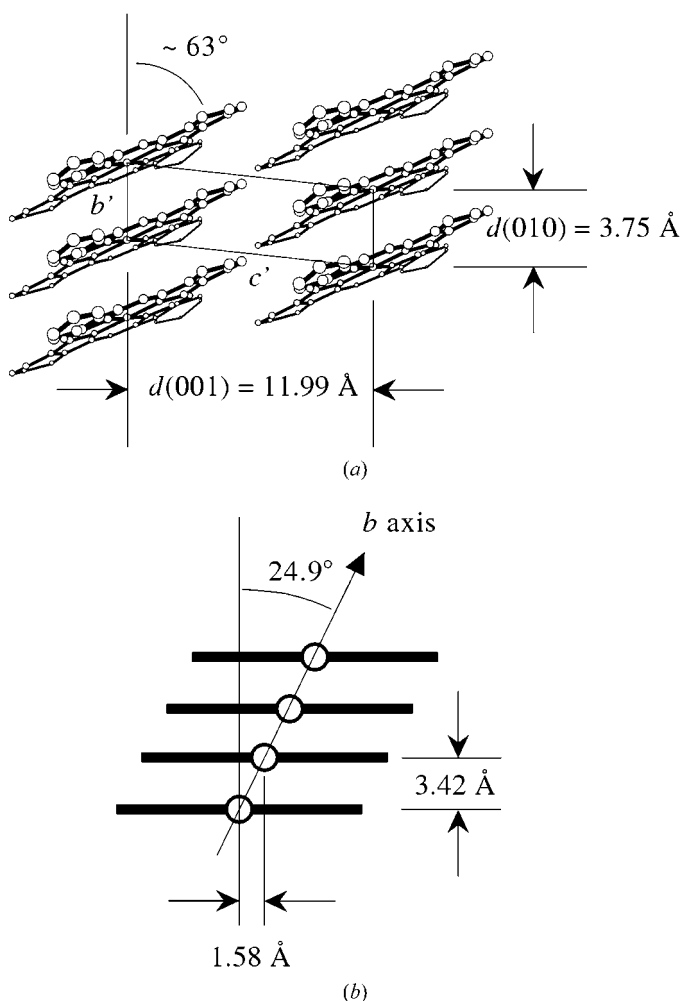

Figure 9
(*a*) Top and (*c*) side views of the molecular structure obtained from Refinement I, respectively, and (*b*) and (*d*) from Refinement II.

know whether only one of the proposed structures is correct or if two types of polymorph exist; further investigation is needed.

The $\alpha(\times)$-group contains two distinct types of crystal structure. α-PtPc and γ-PtPc (Brown, 1968*b*) belong to this group and their crystal structures are different from each other, although both have a herringbone-type molecular arrangement. α-H$_2$Pc (Janczak & Kubiak, 1992) is isostructural with α-PtPc. γ-CuPc (Eastes, 1956) also belongs to this group.

Since each group has only one or two types of crystal structure, our classification can be helpful for reducing the confusion surrounding the nomenclature of polymorphs and for understanding the diversity of the polymorphs of planar phthalocyanines.

Lastly, we comment on the crystal structure of α-CoPc reported by Ballirano *et al.* (1998) since its powder X-ray profile and lattice constants are quite similar to our result for α-CuPc: $P\bar{1}$, $Z = 1$, $a = 12.090$, $b = 3.754$, $c = 12.800$ Å, $\alpha = 88.96$, $\beta = 90.97$ and $\gamma = 95.09°$. If we take $\mathbf{a}' = -\mathbf{c}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = \mathbf{a}$ as new axes of α-CoPc, the lattice constants become: $a' = 12.800$,

$b' = 3.754$, $c' = 12.090$ Å, $\alpha' = 95.09°$, $\beta' = 89.03°$ and $\gamma' = 91.04°$, which are almost the same as those of α-CuPc. However, the molecular stacking mode of α-CoPc is the $\alpha(\times)$-type on the basis of the lattice constants and atomic coordinates they reported. As our Rietveld analysis has demonstrated, both Model I [$\alpha(\times)$-stacking] and Model II [($\alpha(+)$-stacking] led to fairly small R values in the case of α-CuPc. If they had started Rietveld analysis from another structural model they might have had smaller R factors. Further investigations are needed of the crystal structure of α-CoPc.

5. Conclusions

After the long period of misunderstanding and confusion, the crystal structure of α-CuPc has been finally determined. α-CuPc is neither isostructural with α-H$_2$Pc nor α-PtPc. Although it has almost the same length of the shortest lattice axis as those of α-H$_2$Pc and α-PtPc, the molecular offset direction of α-CuPc within a molecular column is different by $\sim$45° from those of α-H$_2$Pc, α-PtPc and β-modifications of various phthalocyanines. This offset direction is the same as that of χ-H$_2$Pc. On the basis of these findings, the crystal structures of various planar phthalocyanines having columnar structures have been classified into four types in terms of molecular stacking mode within a molecular column. This

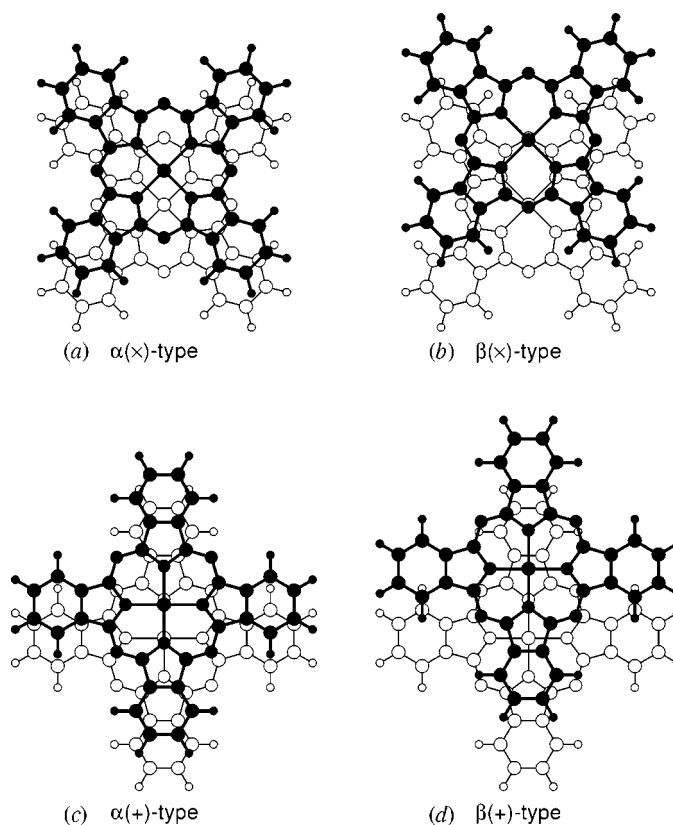

Figure 10
(*a*) *a*-axis projection of the crystal structure of α-CuPc. (*b*) Schematic representation of the molecular stacking of α-CuPc.

(*a*) $\alpha(\times)$-type   (*b*) $\beta(\times)$-type

(*c*) $\alpha(+)$-type   (*d*) $\beta(+)$-type

Figure 11
A classification of the stacking modes of planar phthalocyanines within a molecular column.

classification can be helpful for understanding the polymorphism of the phthalocyanines.

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