research papers

Diffuse X-ray scattering and reverse Monte Carlo simulation of the short-range order in ytterbium iodine phthalocyanine [YbPc$_2$]I$_2$

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Iodine-doped ytterbium phthalocyanine, C$_{64}$H$_{32}$N$_{16}$YbI$_2$, [YbPc$_2$]I$_2$ (YPI), presents an example of a disordered modulated crystal structure of the intergrowth type. The short-range order in YPI has been studied at ambient temperature by the diffuse X-ray scattering technique. Both Yb and I atoms are disordered. In a unit cell of the average structure, the Yb atoms occupy two positions, $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ or $\frac{1}{2}, \frac{1}{2}, \frac{3}{4}$, with occupancy 0.5. In the neighbouring unit cells in the (001) plane there is, however, a strong tendency towards an alternating distribution of ytterbium in positions shifted by $\Delta z = \frac{1}{2}$. The crystal structure of YPI consists of one-dimensional columnar stacks of [YbPc$_2^{2/3+}$]$_n$ and of linear iodine chains [I$_3^-$]$_n$. The modulation is commensurate since the period c_I of iodine chains [I$_3^-$]$_n$ in the [001] direction is equal to one-half of the period c of the [YbPc$_2^{2/3+}$]$_n$ stacks. In the crystal structure, each stack of [YbPc$_2^{2/3+}$]$_n$ may occur in two settings shifted by $c/2$ and each iodine chain in three settings shifted along [001] by one-third of the period c_I. The short-range order of iodine chains distributed over three settings results in a complicated pattern. Iodine chains of the same setting tend to form ribbons perpendicular to $\langle 100 \rangle$ and running along [001].

1. Introduction

The development of automatic single-crystal diffractometers with two-dimensional CCD detectors opens new perspectives in crystal structure analysis. Data collection performed with a CCD diffractometer yields an enormous amount of information on the diffraction pattern in the whole reciprocal lattice. The diffraction pattern in between the reciprocal lattice points, usually neglected in routine crystal structure analysis, contains information about the short-range order in disordered crystal structures.

Iodine-doped ytterbium phthalocyanine ([YbPc$_2$]I$_2$), in short YPI, is a member of the family of tetragonal iodine-doped metal phthalocyanines [(AsPc)Pc]I$_2$ (Janczak *et al.*, 1999), [UPc$_2$]I$_2$ (Janczak *et al.*, 2000), [UPc$_2$]I$_{5/3}$ (Janczak & Kubiak, 1999), [TiPc$_2$]I$_2$ (Capobianchi *et al.*, 1993), [SnPc$_2$]I$_2$ (Capobianchi *et al.*, 1993), and [BiPc$_2$]I$_{1.5}$ (Janczak *et al.*, 1998).

The crystal structure of YPI was determined in the *P*4/*mcc* space group with one molecule per tetragonal unit cell with a = 13.927 (2) Å and c = 6.409 (1) Å (Janczak *et al.*, 1999). Partially oxidized planar phthalocyanine rings are located at the mirror planes perpendicular to [001] with $z = 0$ and $z = \frac{1}{2}$. Iodine atoms constitute linear I$_3^-$ anions arranged in chains [I$_3^-$]$_n$ running along [001]. Therefore, the chemical composition of iodine-doped ytterbium phthalocyanine may be more precisely expressed by the formula [YbPc$_2$](I$_3$)$_{2/3}$.

According to Janczak *et al.* (1999), both Yb and I atoms are disordered. In the average crystal structure, Yb atoms are

located between phthalocyanine rings in the Wyckoff positions $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{2}, \frac{1}{2}, \frac{3}{4}$ with occupancy 0.5. The period c_I of iodine chains in the [001] direction is equal to 1.5 times the lattice parameter c of the averaged unit cell. The iodine chains are arranged at random in three different settings with respect to the one-dimensional columnar stacks of $[YbPc_2^{2/3+}]_n$. I atoms form linear $(I-I-I)^-$ anions (in short I_3^-). The central I atoms may be located with equal probability at $z_I c_I = 0.25c$, $0.75c$ or $1.25c$. The crystal structure of YPI in projection along [001] is presented in Fig. 1.

The crystal structure of YPI may be regarded as consisting of one-dimensional columnar stacks of $[YbPc_2^{2/3+}]_n$ and of linear iodine chains $[I_3^-]_n$. Each stack of $[YbPc_2^{2/3+}]_n$ may occur in two settings shifted by $c/2$ and each iodine chain in three settings shown in Figs. 2(a) and 2(b).

In the case of ordered iodine chains (all chains in the same setting), YPI would constitute a commensurate modulated crystal structure of the intergrowth type with two partly overlapping unit cells: a, b, c and $a_I = a$, $b_I = b$, $c_I = 3c/2$ for columnar stacks $[YbPc_2^{2/3+}]_n$ and iodine chains $[I_3^-]_n$, respectively. If all iodine chains were of the same setting, a double periodicity in the [001] direction would result in additional sharp hkl_I Bragg reflections at the lattice points of the reciprocal lattice $a_I^* = a^*$, $b_I^* = b^*$ and $c_I^* = 2c^*/3$. In the case of complete disorder and random distribution of iodine chains over three settings, the hkl_I reciprocal lattice planes would be replaced by sheets of diffuse scattering. Closer inspection of the hkl_I layers reveals that they consist of very diffuse spots indicating short-range order of iodine chains in the crystal structure of YPI.

2. Experimental

Crystals of $[YbPc_2]I_2$ were obtained by the reaction of pure powdered ytterbium and 1,2-dicyanobenzene under a stream of iodine (Janczak *et al.*, 1999). Diffuse X-ray scattering patterns were recorded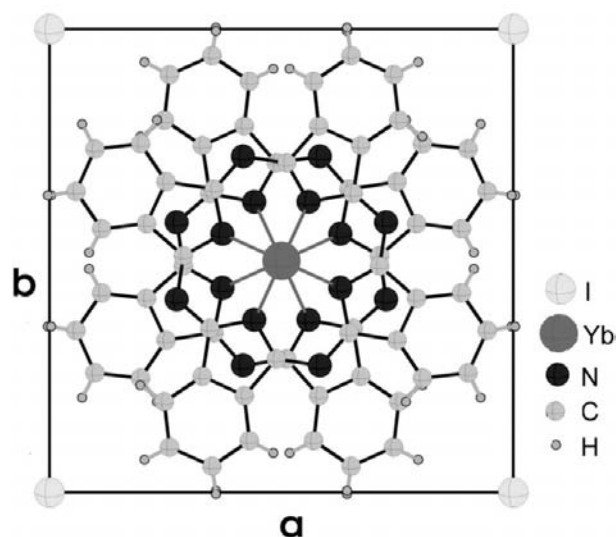 for YPI using a KUMA Diffraction KM4CCD single-crystal automatic diffractometer with a two-dimensional position-sensitive CCD detector. Graphite monochromated Mo $K\alpha$ X-rays with $\lambda = 0.71073$ Å were generated at 43 kV and 23 mA.

Diffuse scattering could be observed easily on the rotation patterns recorded by the CCD detector and were displayed on the monitor screen (Figs. 3a and 3b). Data collection was similar to that employed in routine crystal structure determination. It was possible to limit the scanning to lower θ angles because at higher angles diffuse scattering was hardly visible. However, we have increased exposure times because diffuse scattering is a few orders of magnitude weaker than Bragg reflections.

Rotation patterns (Figs. 3a and 3b) were obtained by recording the diffracted X-rays from the crystal rotated by 25° for about 4 min. They are presented in the colour palette used by the KUMA Diffraction program (Meyer, 2002). The full set of X-ray diffraction data was collected over the range 3–96° in 2θ in ten runs with $\Delta\omega = 0.5°$ and longer than usual measuring time $t = 30$ s. Measured intensities were recorded in 1769 frames, each frame consisting of 512×512 pixels.
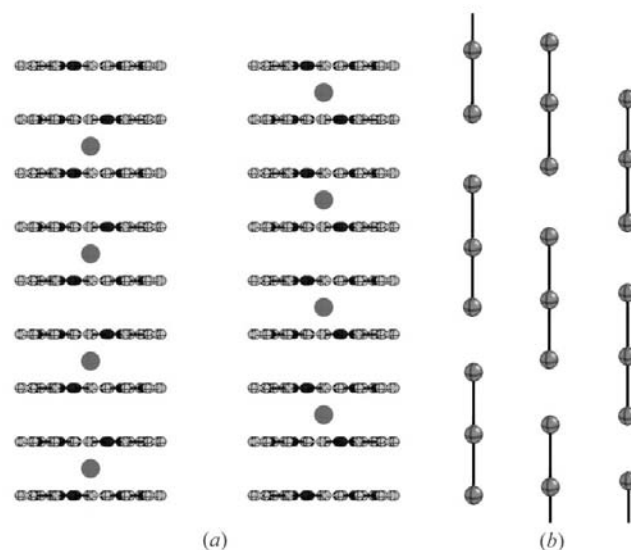

Figure 2
Components of the crystal structure of YPI: (a) one-dimensional columnar stacks of $[YbPc_2]_n$ in two settings and (b) linear iodine chains $[I_3^-]_n$ in three settings.

Figure 1
The crystal structure of YPI in projection along [001] according to Janczak *et al.* (1999).
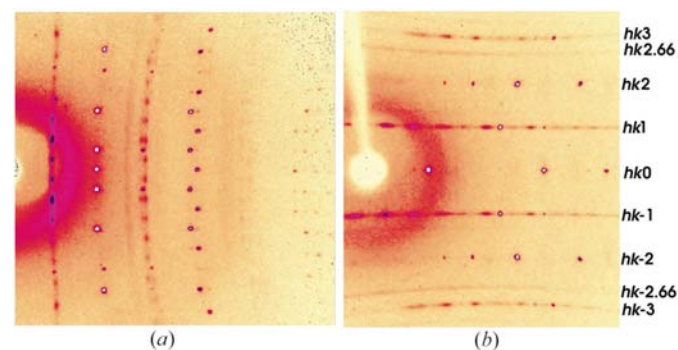

Figure 3
Rotation patterns of YPI: (a) [100] and (b) [001].

3. Results and discussion

Diffuse scattering of YPI is localized in the reciprocal lattice in the l layers of the average crystal structure and in the l_I layers owing to iodine chains $[I_3^-]_n$. From the relation $c_I^* = 2c^*/3$, it follows that in the case of l even the layers l and l_I do overlap. In order to avoid misunderstanding, we shall keep to the reciprocal lattice of the average structure, denoting the non-overlapping layers of iodine chains by non-integer numbers.

It is convenient to qualitatively check the short-range order in crystals by taking X-ray rotation photographs. The CCD diffractometer allows one to display on the monitor screen rotation patterns similar to conventional oscillation photographs. The rotation pattern [001] (Fig. 3b) of YPI contains hkL layers with $L = 0, 1, 2, 2.66$ and 3. The layers are of three kinds: (i) hkL layers with L even, consisting of sharp Bragg reflections of the average structure; (ii) hkL layers with L odd, consisting of Bragg reflections accompanied by diffuse superstructure reflections owing to the local order of ytterbium and (iii) hkL layers with L non-integer, which present apparently continuous streaks consisting of very diffuse spots due to iodine chains.

More information could be obtained using Meyer's (2002) program for reconstruction of single layers of the reciprocal lattice from the full set of intensity data. The consecutive reciprocal lattice $1kL$ lines with $L = 2, 2.66, 3, 4.66, 5$ and 6 can be seen in the $1kl$ section of the reciprocal lattice (Fig. 4). Lines with $L = 3.33$ and 5.33 were too weak to be observed.

YPI presents an interesting example of a crystal structure with two kinds of disorder, different and apparently independent for Yb atoms and iodine chains, respectively. Fortunately, both kinds of disorder are manifested in different regions of the reciprocal space. Moreover, diffuse reflections due to disorder of both Yb atoms and iodine chains are localized in definite layers in the reciprocal space, which

allowed us to reduce the problem to the two-dimensional case and to study both kinds of disorder independently.

We have made the following assumptions:

(i) Both one-dimensional columnar stacks $[YbPc_2^{2/3+}]_n$ and single iodine chains are ordered – there is no disorder in the [001] direction. It is sufficient, therefore, to consider the distribution in the crystal structure of columnar stacks of $[YbPc_2^{2/3+}]_n$ in two settings and of linear iodine chains $[I_3^-]_n$ in three settings.

(ii) Owing to different periods in the [001] direction, the short-range order of Yb does not depend on the local arrangement of iodine chains and *vice versa*.

(iii) The distributions of ytterbium and iodine chains therefore may be studied independently.

The first assumption is based on observations that the line widths in the [001] direction of the diffuse streaks and of the diffuse reflections are comparable to the line width of Bragg reflections. The next two assumptions follow from the observation that the disorder of Yb atoms results in the superstructure diffuse spots localized in hkL layers with odd L, while diffuse X-ray scattering resultant from disorder of the iodine chains forms separate hkL layers with non-integer L.

From these assumptions, it also follows that the short-range order and pair correlation coefficients of ytterbium may be studied and determined by the reverse Monte Carlo (RMC) simulation of a single hkL layer with odd L, while the short-range order of iodine chains can be determined by RMC simulation of a single hkL layer with non-integer L.

The RMC simulations were carried out using the program *DISCUS* (Proffen & Neder, 1997). The layer $hk1$ (Fig. 5a) was reconstructed from the measured intensity data. It was simulated (Fig. 5b) by changing the distribution of Yb atoms in a set of $94 \times 94 \times 1$ unit cells arranged in plane (001). A random distribution of Yb atoms (Fig. 6a) located at $z = \frac{1}{4}$ (full circles) or at $z = \frac{3}{4}$ (empty circles) was used as a starting point in the simulation procedure. After about 25 000 cycles of the RMC, no further improvement in the agreement indicated the accomplishment of the simulation. Fig. 6(b) presents the distribution of Yb atoms after the RMC simulation. The distribution of Yb calculated by the RMC simulation of other hkL layers with L odd, as well as simultaneous simulation of a few layers, produced similar results.
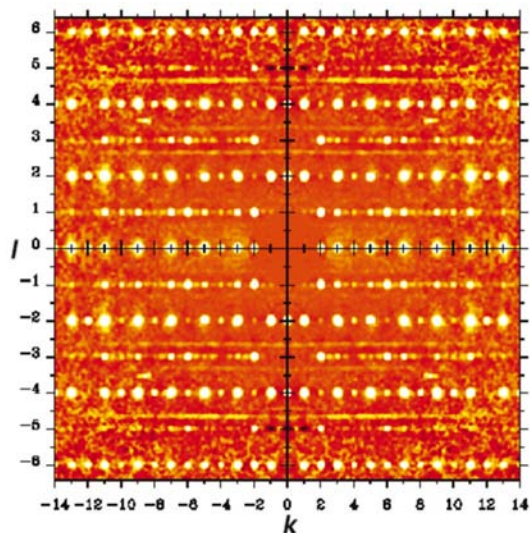

Figure 4
Diffuse scattering of YPI. Cross section of the reciprocal lattice through the layer $1kl$.
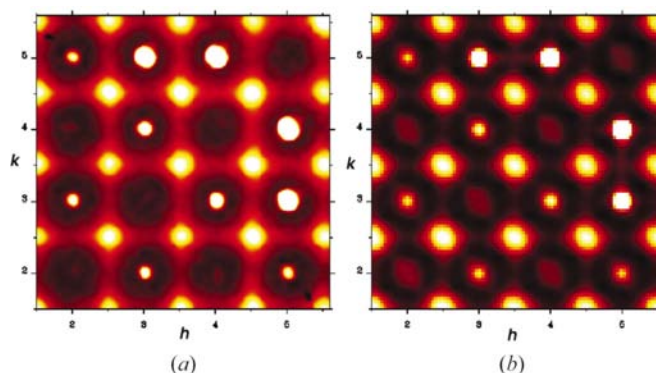

Figure 5
Diffuse scattering of YPI, layer $hk1$: (a) measured, (b) simulated.

Table 1
Correlations $c\langle uvw \rangle$ calculated for Yb atoms.

Model size $94 \times 94 \times 1$ unit cells. Y = Yb atom at $z = \frac{1}{4}$, V = Yb atom at $\frac{3}{4}$. Total number of pairs $(YY + VV + YV + VY) = 35344$.

Distance/neighbours	YY	YV + VY	VV	$c\langle uvw \rangle$
$\langle 100 \rangle$	15.67%	68.67%	15.65%	−0.3735
$\langle 110 \rangle$	34.83%	30.35%	34.81%	0.3929
$\langle 200 \rangle$	31.45%	37.13%	31.42%	0.2574
$\langle 220 \rangle$	26.92%	46.17%	26.90%	0.0765
$\langle 300 \rangle$	22.62%	54.79%	22.60%	−0.0957
$\langle 330 \rangle$	25.16%	49.69%	25.14%	0.0061
$\langle 400 \rangle$	25.47%	49.08%	25.45%	0.0183
$\langle 440 \rangle$	24.95%	50.12%	24.93%	−0.0025

Table 2
Correlations $c\langle uvw \rangle$ calculated by RMC for iodine chains in A, B and C setting.

$D = B$ or C. Model size $94 \times 94 \times 3$ unit cells. Total number of pairs $(AA + DD + AD + DA) = 106\,032$.

Distance/neighbours	AA	AD + DA	DD	$c\langle uvw \rangle$
$\langle 100 \rangle$	13.42%	39.12%	47.46%	0.1150
$\langle 110 \rangle$	5.63%	54.70%	39.67%	−0.2373
$\langle 200 \rangle$	13.77%	38.41%	47.82%	0.1311
$\langle 220 \rangle$	12.15%	41.65%	46.20%	0.0579
$\langle 300 \rangle$	11.56%	42.85%	45.60%	0.0307
$\langle 330 \rangle$	10.48%	45.00%	44.52%	−0.0179
$\langle 400 \rangle$	11.46%	43.03%	45.51%	0.0266
$\langle 440 \rangle$	10.92%	44.13%	44.96%	0.0018

Pair correlation coefficients $c\langle uvw \rangle$ between pairs of sites occupied by Yb atoms separated by $\langle uvw \rangle$ were calculated as

$$c\langle uvw \rangle = \frac{P\langle uvw \rangle - \theta^2}{\theta(1 - \theta)}.$$

θ is an overall occupancy of Yb and $P\langle uvw \rangle$ is the joint probability that both sites separated by $\langle uvw \rangle$ are occupied by Yb at $z = \frac{1}{4}$,

$$P\langle uvw \rangle = YY/(YY + VV + YV + VY),$$

where YY is the number of pairs of sites separated by $\langle uvw \rangle$ and occupied by Yb at $z = \frac{1}{4}$, VV is the corresponding number for Yb atoms at $z = \frac{3}{4}$, while $YV + VY$ is the number of pairs of sites occupied by Yb at different z values. Pair correlation coefficients $c\langle uvw \rangle$ for Yb atoms are presented in Table 1.

Diffuse X-ray scattering by iodine chains $[I_3^-]_n$ observed in the layers $hk2.66$ and $hk4.66$ as apparently continuous streaks (Figs. 3b and 4) indicated substantial disorder. However, the reconstruction of the layer $hk2.66$ revealed a set of diffuse reflections (Fig. 7a). The RMC simulation of this layer (Fig. 7b) allowed us to determine the short-range order of iodine chains. A structure model consisting of a set of $94 \times 94 \times 3$ unit cells arranged in plane (001) was used for the simulation. A random distribution of iodine chains of different settings marked in three colours (Fig. 8a) was used as the starting point in the simulation procedure. About 25 000 cycles
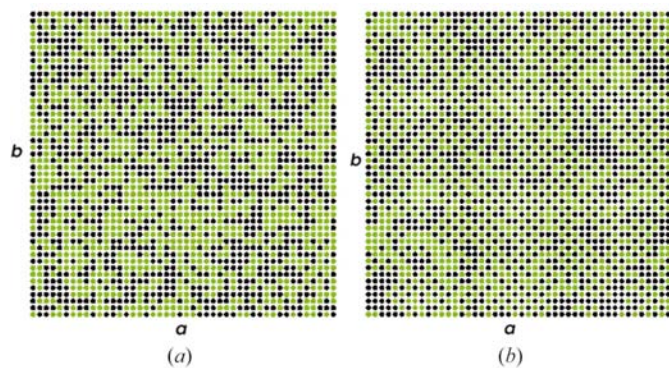
of the RMC proved to be sufficient to accomplish the simulation. The distribution of iodine chains after simulation is presented in Fig. 8(b). Pair correlation coefficients $c\langle uvw \rangle$ between pairs of iodine chains of the same setting (in this case setting A) separated by $\langle 100 \rangle$ and $\langle 110 \rangle$ are collected in Table 2.

In the cases of both Yb atoms and iodine chains, the simulated layers were restricted to about 5×5 reciprocal unit cells. Calculations for larger areas (14×14 reciprocal unit cells) produced similar results.
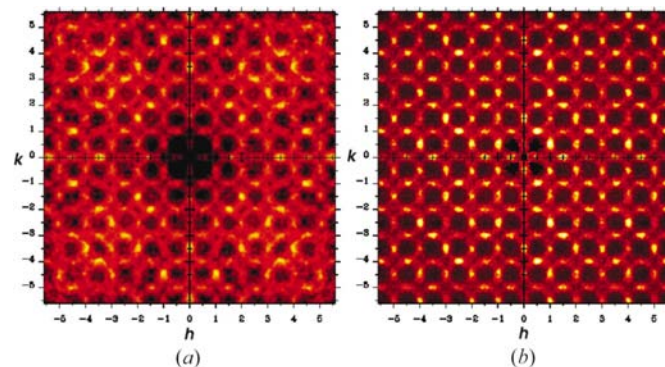

Figure 7
Diffuse scattering of YPI, layer $hk2.66$: (a) measured, (b) simulated.

Figure 6
Distribution of Yb atoms in the layer x, y, $0 \geq z > 1$: (a) random distribution and (b) with the short-range order revealed by RMC. Empty circles: Yb at $z = \frac{1}{4}$. Full circles: Yb at $z = \frac{3}{4}$.
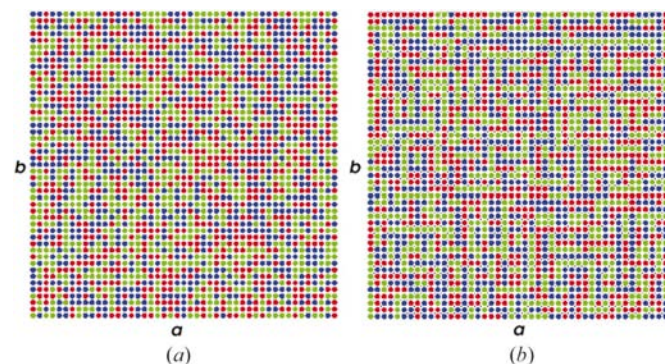

Figure 8
Distribution of iodine chains over three settings marked by three colours: (a) random distribution, (b) with the short-range order revealed by RMC.

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4. Concluding remarks

The crystal structure of iodine-doped ytterbium phthalocyanine, YPI, presents an example of a disordered modulated crystal structure of intergrowth type. The modulation is commensurate since the period c_I of iodine chains $[I_3^-]_n$ in the [001] direction is equal to 1.5 times the [001] period of one-dimensional columnar stacks of $[YbPc_2^{2/3+}]_n$ and of the averaged unit cell c. YPI is also an example of independent short-range ordering of two structure components: columnar stacks $[YbPc_2^{2/3+}]_n$ and linear iodine chains $[I_3^-]_n$.

In the neighbouring unit cells separated by $\langle 100 \rangle$ there is a strong tendency towards an alternating arrangement of $[YbPc_2^{2/3+}]_n$ stacks of two settings, which is equivalent to the distribution of ytterbium ions in positions shifted by $\Delta z = \frac{1}{2}$. This is understandable because repulsive forces between Yb^{3+} ions make greater distances energetically favourable. Table 1 presents the correlation coefficients $c\langle uvw \rangle$ calculated for the distribution of Yb atoms. The correlation between the positions of Yb atoms decreases with increasing distance. The correlation coefficients $c\langle 400 \rangle$ and $c\langle 440 \rangle$ become negligible and the distance of the four lattice cells may be accepted as a radius of nanodomains with the ordered distribution of ytterbium.

The alternating ytterbium distribution requires revision of the space-group symmetry of YPI. The space group of the average structure (with long-range averaging) remains $P4/mcc$. The short-range order of Yb implies, however, a crystal structure of YPI consisting of small regions (super-structure anti-phase nanodomains) with tetragonal unit cells: $a' = 2^{1/2}a = 19.696\ (3)$ Å, $c' = c = 6.409\ (1)$ Å and space group $P4/nnc$.

The correlation of iodine chains is quite different. Pair correlation coefficients $c\langle u00 \rangle$ between pairs of iodine chains of the same setting separated by $\langle u00 \rangle$ are positive. In contrast to the ytterbium distribution, iodine chains of the same setting tend to form ribbons running along [001] and perpendicular to $\langle 010 \rangle$. There is no simple explanation for correlation of this kind. There are, however, some hints indicating that in $[(AsPc)Pc]I_2$ (Janczak et al., 1999) and in $[UPc_2]I_{5/3}$ (Janczak & Kubiak, 1999), I_3^- ions are polar. Assuming that $[I_3^-]_n$ chains are also polar in YPI, one can expect an antiparallel distribution of iodine chains of the same setting but different polarity along the $\langle 100 \rangle$ directions, which may explain the apparently strange ordering of iodine chains.

Studies of diffuse scattering and short-range order in $[(AsPc)Pc]I_2$, $[UPc_2]I_2$ and $[UPc_2]I_{5/3}$ are in progress.

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