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Diffraction studies on metal free phthalocyanines (β-H_2Pc and *X*-H_2Pc)

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The crystal structure of the β-polymorph of metal free phthalocyanine (β-H_2Pc) was redetermined from single crystals to obtain precise placements of the hydrogen atoms and a precise model for the *X*-polymorph (*X*-H_2Pc) for which only limited data from different diffraction techniques are available. Partial occupancy for the hydrogens fixed to the nitrogens in the inner ring was found leading to a highly symmetric phthalocyanine molecule. Careful evaluation of X-ray, electron and neutron diffraction data for *X*-H_2Pc results in an orthorhombic unit cell with $a = 2.10$ nm, $b = 0.491$ nm, $c = 2.31$ nm, space group $Pna2_1$ containing four molecules in contrast to a recent determination of Oka and Okada who proposed a monoclinic unit cell with two molecules. As expected the phthalocyanine molecules pack in stacks. The overlap of molecules within one stack matches the current ideas for photosensitive phthalocyanine pigments.

1. Introduction

The structural arrangements of phthalocyanine molecules are of interest, because various polymorphs of the same molecular or of different molecular species exhibit a variety of electronic spectra and adsorb light at different intervals of the ultraviolet to visible (u.v.-vis.) or infrared i.r. wavelength regions due to differences in structure. The molecular crystal structures of several polymorphs of the metal complexed and the metal free phthalocyanines are known by classical single crystal analysis [cf., 1, 2]. The so-called β metal free polymorph (β-H_2Pc) was determined 60 years ago by the pioneering work of Robertson [1]. This structure is now redetermined to obtain precise data with regard to the hydrogen positions, which are a necessity if these molecules are to serve as a model for other polymorphs in neutron diffraction studies.

The structure of the so called *X*-H_2Pc polymorph, which has gained much interest as a photogenerator, has recently been published [3]. In reviewing experimental data collected several years ago, it became clear that these data contradict the published structure that was established by assuming the same space group and number of molecules in the unit cell as for the β-polymorph. Because single crystals are not available for *X*-H_2Pc, the structure has been solved by the above mentioned authors with powder diffraction data applying the Rietveld method.

In recent years, computer modelling of conformation and packing of molecules in conjunction with X-ray fibre, electron and powder diffraction data has proven a useful tool in solving polymer structures of tiny crystallites. This method can also be applied to imperfect structures of so-called "real" organic crystals of small sizes with isotropic or anisotropic disorder in the material. Although analysing complete X-ray powder patterns by the Rietveld method has proven to be quite powerful in the field of mineral structure and composition studies, the method still has some drawbacks, which to some extent lie in the nature of the structure (e.g. unfavourable unit cell dimensions) and might be also due to the fact that the method has not been fully developed for these special cases. The method of packing analysis in combination with X-ray pattern analysis seems, at least at the present time, to be the method of choice for solving the structure of imperfect crystals such as *X*-H_2Pc especially when anisotropic disorder of the material has to be considered and might serve as a phasing model for single crystal analysis when direct methods fail.

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2. Experimental procedure

2.1. Data collection

The data collection for β-H_2Pc was performed on a CAD4 single crystal diffractometer from ENRAF, NONIUS, Delft. The basic crystallographic data are collected in Table I. MoK_α radiation was used for a crystal with the dimensions $0.3 \times 0.15 \times 0.1$ mm^3. Data reduction and all other calculations were carried out on a Micro VAX computer with the MolEN package [4]. Experimental data for X-H_2Pc, which crystallizes in tiny crystals, not suitable for single crystal analysis, are available from various scattering techniques:

1. electron diffraction of these small single crystals,
2. X-ray powder diffraction (Fig. 1a) collected on a Siemens D 5000 instrument with the capability of peak deconvolution,
3. neutron powder diffraction (Fig. 1b) taken at National Institute for Standards and Technology (NIST), and
4. X-ray fibre diffraction obtained by imbedding the elongated tiny single crystal in a polyethylene matrix, casting films and stretching small strips of these films to fibres.

All these data were evaluated to determine the unit cell. The X-ray and neutron powder data were deconvoluted for the determination of the intensity of single peaks where possible. The structure factors were calculated after the necessary reduction for polarization and Lorentz factors.

TABLE I Crystallographic data collected β-H_2Pc and X-H_2Pc

	β-H_2Pc	X-H_2Pc
Temperature, °C	16.5	R.t.
Molecular formula	$C_{16}H_9N_4$	$C_{32}H_{18}N_8$
Formula weight, g mol^{-1}	257.28	514.56
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
Lattice parameters,		electron diffraction
a, nm	1.479 6(6)	2.10(1)
b, nm	0.473 25(6)	0.491(5)
c, nm	1.735 7(7)	2.31(1)
α, deg	90	90
β, deg	104.32(2)	90
γ, deg	90	90
V, nm^3	117.76(7)	238.2
Z	4	4
D_{cal}, g cm^{-3}	1.45	1.44
Reflections for lattice refinement	25	–
Scan range, θ°	9–24	–
F(000)	532	1064
λ(MoK_α) nm	0.071 073	0.155 70(λ$_{\mathrm{neutron}}$)
λ(Cu$K_{\alpha1}$), nm		0.154 06
μ(MoK_α), cm^{-1}	0.8	–
Unique data	2353	21
Scan range, θ°	1–25	3–16
Significant I's (> 3σ)	1553	–
Parameters refined	181	6
R	0.037	0.18(overall B)
R_{w}	0.045	0.26(overall B)
Highest peak in ΔF map	0.15(6)	–
Crystal size, mm^3	$0.3 \times 0.15 \times 0.1$	Powder

2.2. Unit cell and space group determination

2.2.1. *β-H_2Pc*

Twenty-five reflections in the theta-range from 9 to 25° were used for the determination of the monoclinic unit cell containing two molecules. The result of

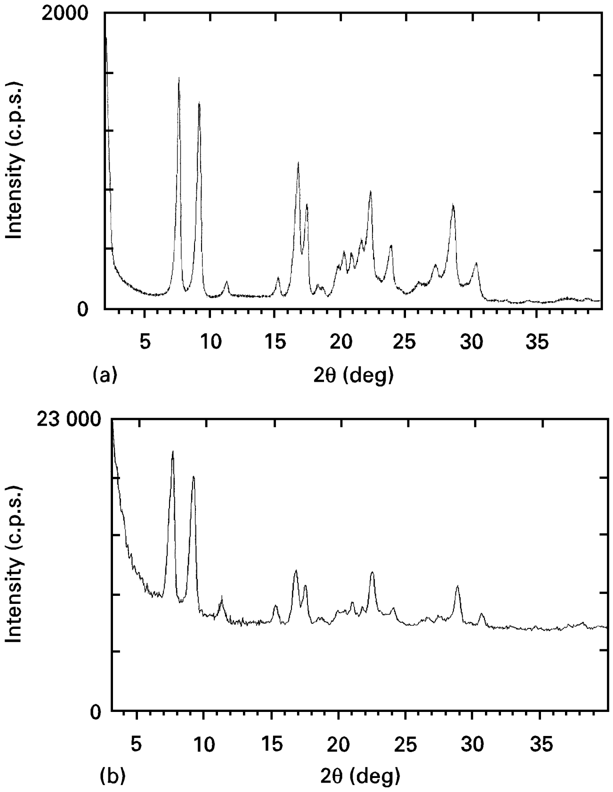

Figure 1 X-ray (a) and neutron (b) powder diffraction diagram of X-H_2Pc (c.p.s.: counts per step).

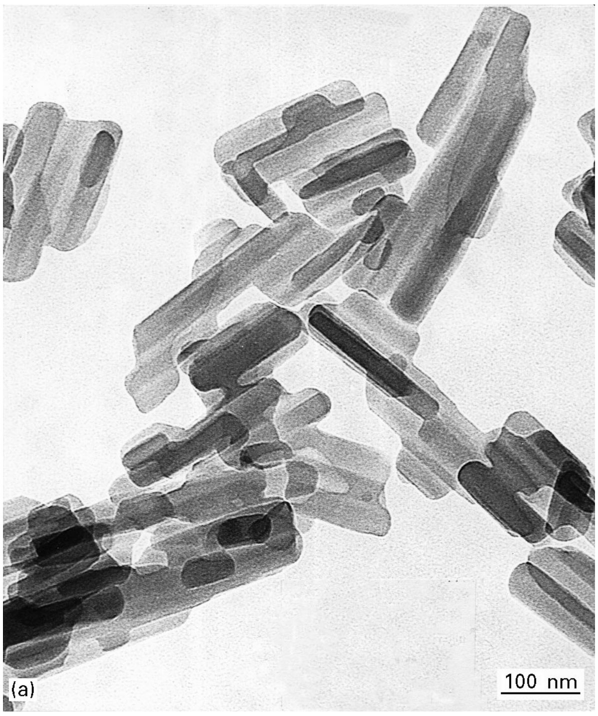

Figure 2 (a) Electron micrograph of tiny single crystals of X-H_2Pc, and (b) their electron diffractogram at different tilt angles (zero, ±12°, etc.).

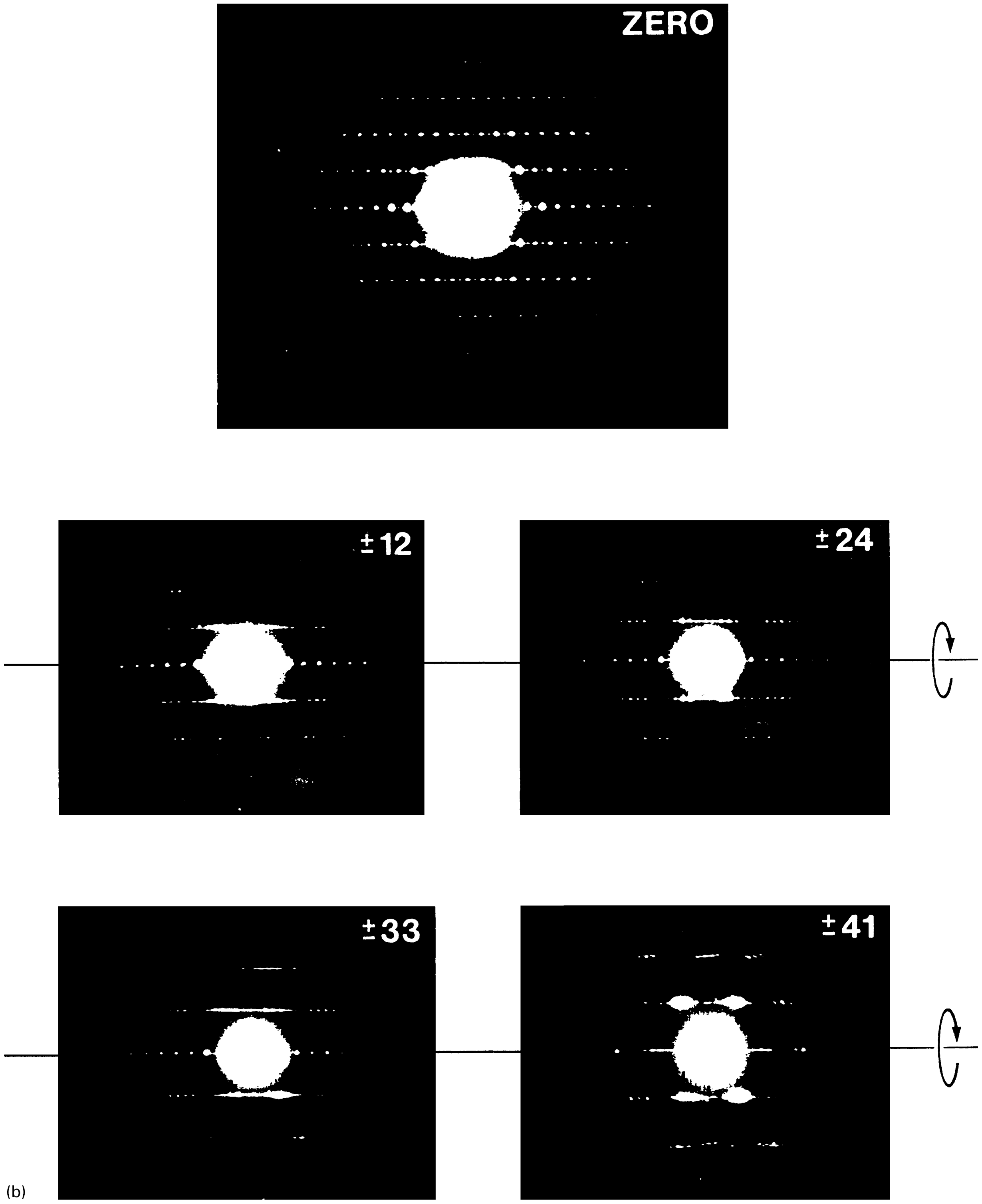

Figure 2 (continued).

a weighted least squares procedure is listed in Table I. Systematic absences led to space group $P2_1/n$.

2.2.2. *X-H$_2$Pc*

Excellent electron diffraction patterns from tiny single crystals (Fig. 2a, b) held on gold coated grids for calibration purposes led to the evaluation of a unit cell projection in two dimensions with $b = 0.491$ nm, $c = 2.31$ nm, $\alpha = 90°$, possible plane groups are $c2mm$, $c2m$ or pgg from systematic absences of reflections. The third dimension was obtained by an evaluation of X-ray powder and fibre patterns as $a = 2.10$ nm, $\beta = \gamma = 90°$. This orthorhombic unit cell contains four molecules with the following absences of reflections determined by electron diffraction in the b–c plane, electron diffraction on tilted samples (tilt axis is c), and by X-ray and neutron powder diffraction: $0kl$: $k + 1 = 2n$; $h0l$: $h = 2n$; $hk0$: no conditions. These systematic absences lead to the acentric space group

Pna2_1, (with four molecules) or to the centric space group *Pnma* (with eight molecules or four molecules on special positions, which would then suit the measured density). *Pnma* could be excluded on potential energy considerations (many short contacts, if a reasonable by X-ray analysis confirmed projection of the molecules onto the *a*–*c* plane is considered).

The *a* and *c* dimensions of the X-ray or neutron diffraction pattern agree with the electron diffraction data and indicate the presence of a subcell in the *b*-projection containing two molecules with $a' = a/2$ and $c' = c$ supporting the choice of a space group for which the same subgroup is obtained. The measured and calculated densities are in agreement ($\rho_{ex} = 1.45\ \mathrm{g\,cm^{-3}}$).

2.3. Crystal structure determination

2.3.1. β-H_2Pc

The starting model was obtained by direct methods and refined including all hydrogens found by difference Fourier procedure to $R = 0.038$ (Fig. 3, Table II). The average C–H bond length resulted in 0.097 nm, for N–H in 0.085 nm. For molecular modelling calculations as well as for comparing with neutron scattering data, the average bond length for C–H was placed at 0.105 nm and N–H to 0.09 nm. A last refinement cycle with these bond lengths fixed lead to $R = 0.037$. The difference Fourier map excluding the hydrogens fixed to the nitrogens at the inner ring showed electron densities on each possible side at the inner ring and, because the bond distances for N1–C8, N1–C1 and N2–C9, N2–C16 are all equal, partial occupancy with 0.5 H for each possible site was assumed in the final calculations. These N–C bonds are about 0.004 nm longer than those at the outer ring (Table III).

The phthalocyanine molecule possesses a planar conformation, because all torsion angles deviate less than 2° from 0° or 180°.

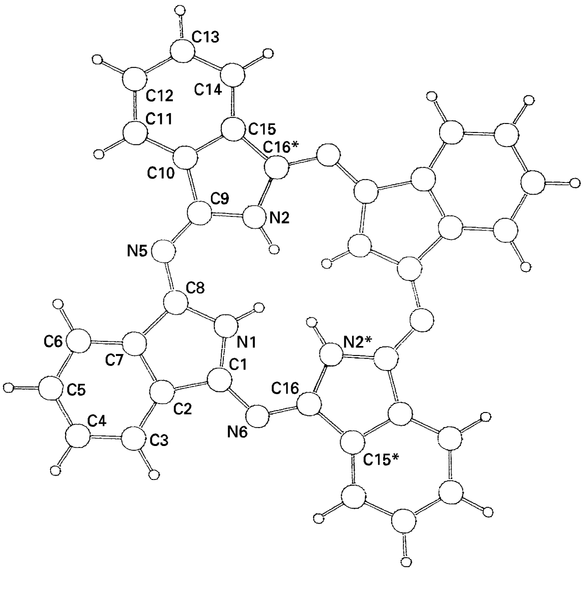

Figure 3 Representation of the β-H_2Pc molecule and numbering of atoms.

TABLE II Positional parameters (fractional coordinates), B_{eq} values and their estimated standard deviations for β-H_2Pc

Atom	Crystallographic directions			*B* (nm^2)
	x	*y*	*z*	
N1	0.89948(8)	0.1933(3)	1.03465(7)	0.258(3)
N2	0.97630(8)	0.2180(3)	0.90016(7)	0.261(3)
N5	0.84735(8)	0.5013(3)	0.92067(7)	0.272(3)
N6	1.09294(8)	0.0273(3)	0.83801(7)	0.270(3)
C1	0.8711(1)	0.1504(4)	1.10309(9)	0.255(3)
C2	0.7919(1)	0.3346(4)	1.10313(9)	0.261(3)
C3	0.7369(1)	0.3727(4)	1.1565(1)	0.322(3)
C4	0.6654(1)	0.5689(4)	1.1370(1)	0.364(4)
C5	0.6490(1)	0.7223(4)	1.0665(1)	0.372(4)
C6	0.7038(1)	0.6864(4)	1.0130(1)	0.318(3)
C7	0.7752(1)	0.4890(4)	1.03250(9)	0.261(3)
C8	0.8442(1)	0.3965(4)	0.99067(9)	0.253(3)
C9	0.9074(1)	0.4173(4)	0.88015(9)	0.251(3)
C10	0.9075(1)	0.5289(4)	0.80236(9)	0.258(3)
C11	0.8513(1)	0.7309(4)	0.7552(1)	0.315(4)
C12	0.8682(1)	0.7899(4)	0.6822(1)	0.355(4)
C13	0.9394(1)	0.6518(4)	0.65705(9)	0.359(4)
C14	0.9960(1)	0.4523(4)	0.70380(9)	0.320(4)
C15	0.9789(1)	0.3920(4)	0.77727(9)	0.255(3)
C16	1.0218(1)	0.1956(3)	0.84032(9)	0.247(3)
H3	0.749	0.257	1.210	0.42[a]
H4	0.623	0.603	1.176	0.47[a]
H5	0.594	0.869	1.054	0.48[a]
H6	0.692	0.803	0.960	0.41[a]
H11	0.798	0.835	0.775	0.41[a]
H12	0.827	0.941	0.645	0.46[a]
H13	0.950	0.701	0.601	0.47[a]
H14	1.050	0.351	0.635	0.41[a]
H1N	0.949	0.098	1.020	0.34[a]
H2N	0.990	0.111	0.943	0.34[a]

[a] The position and isotropic *B* value are fixed for the hydrogens during refinement H1N and H2N: partial occupancy 0.5.

TABLE III Bond distances of β-H_2Pc

Atom 1	Atom 2	Distance (nm)
N1	C1	0.1370(2)
N1	C8	0.1367(2)
N2	C9	0.1369(2)
N2	C16	0.1374(2)
N5	C8	0.1324(2)
N5	C9	0.1323(2)
N6	C16	0.1328(2)
C1	C2	0.1459(2)
C2	C3	0.1387(3)
C2	C7	0.1396(2)
C3	C4	0.1385(2)
C4	C5	0.1392(3)
C5	C6	0.1387(3)
C6	C7	0.1388(2)
C7	C8	0.1458(2)
C9	C10	0.1451(2)
C10	C11	0.1392(2)
C10	C15	0.1397(2)
C11	C12	0.1380(3)
C12	C13	0.1398(3)
C13	C14	0.1384(2)
C14	C15	0.1391(2)
C15	C16	0.1457(2)

2.3.2. X-H_2Pc

The available modelling program for packing and X-ray analysis of small molecules was adapted to the special needs and modified to run on a PC [5]. The starting model for X-H_2Pc was obtained by using the co-ordinates of β-H_2Pc. All H_2Pcs so far known form columns along one unit cell direction, normally the *b* axis with different stacking distances (*b*-dimension), e.g. 0.472 nm for β-H_2Pc and 0.491 nm for X-H_2Pc. The angle between the plane in which the molecule is placed and the stacking direction can easily be calculated taking into account the spacing of two adjacent phthalocyanine molecules of approximately 0.34 nm. This setting angle with respect to *b* amounts to 46° for X-H_2Pc and 42° for β-H_2Pc and can be as low as 26° for other metal free phthalocyanine polymorphs. These differences in stacking as well as rotations of the whole molecule lead to a different π-electron overlap and consequently to the differences in the electronic spectra for various polymorphs.

Subsequently, the stacks were projected onto the *a*–*c* plane, placed in the corner and centre of the planar subcell of $Pna2_1$, ($a' = a/2$; $c' = c$) and refined versus the two-dimensional X-ray or neutron scattering data up to the *d*-spacing of 0.49 nm, that is the first possible appearance of reflections from the third dimension in the X-ray or neutron powder diagram, by only allowing rotations of the molecules within the stacks. An excellent agreement of calculated and observed neutron and X-ray data was obtained and used as a starting model for a full three-dimensional refinement with all experimental data available. The refinement with the neutron powder data is preferred because of higher resolution of the data and especially because of better deconvolution at higher diffraction angles resulting from pure Gaussian profiles of the reflections. For the three-dimensional refinement the molecule of the β-H_2Pc was kept fixed and only rotated around the three axes of the co-ordinate system at the given position, because it had been established by preliminary calculations that the whole molecule was shifted very little for the best fit. With this procedure the parameter to data ratio was improved. Potential energy calculations were also carried out to evaluate the goodness of the fit. The minimum of potential energy appears to be very shallow with the potential energy parameters used and somewhat apart from the refined structure. However, the magnitude of the potential energy for the determined structure is very similar to the one obtained for X-ray structure of β-H_2Pc that also was not positioned in the minimum and no unreasonable short contacts were encountered. The final R values in structure factor refinements for X-ray and neutron diffraction analysis were $R = 17$ and 18%, respectively (Table I) with some overlapping reflections taken into the calculations.

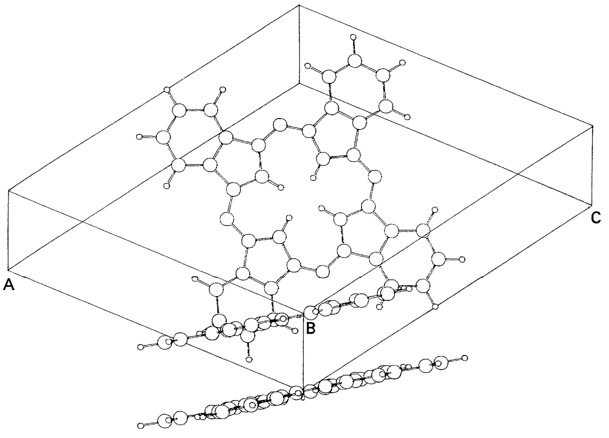

Figure 4 Representation of the packing of β-H_2Pc in space group $P2_1/n$.

TABLE IV Bond angles of β-H_2Pc

Atom 1	Atom 2	Atom 3	Angle (deg)
C1	N1	C8	108.6(1)
C9	N2	C16	109.5(1)
C8	N5	C9	123.8(1)
N1	C1	C2	109.3(1)
C1	C2	C3	132.9(1)
C1	C2	C7	106.3(1)
C3	C2	C7	120.8(1)
C2	C3	C4	117.6(2)
C3	C4	C5	121.4(2)
C4	C5	C6	121.5(2)
C5	C6	C7	117.0(2)
C2	C7	C6	121.7(2)
C2	C7	C8	106.6(1)
C6	C7	C8	131.6(2)
N1	C8	N5	128.7(2)
N1	C8	C7	109.2(1)
N5	C8	C7	122.2(1)
N2	C9	N5	126.9(1)
N2	C9	C10	108.4(1)
N5	C9	C10	122.7(1)
C9	C10	C11	131.3(2)
C9	C10	C15	107.2(1)
C11	C10	C15	121.5(2)
C10	C11	C12	117.6(2)
C11	C12	C13	120.9(2)
C12	C13	C14	122.9(2)
C13	C14	C15	117.2(2)
C10	C15	C14	120.9(1)
C10	C15	C16	106.5(1)
C14	C15	C16	132.6(2)
N2	C16	N6	127.5(1)
N2	C16	C15	108.4(1)
N6	C16	C15	124.1(1)

3. Results and discussion

3.1. β-H_2Pc

The conformation and the numbering of atoms is represented in Fig. 3, the packing within the unit cell in Fig. 4. The fractional atomic co-ordinates are listed in Table II, the bond lengths, angles and torsion angles in Table III–V, respectively. The C–N bonds of the inner ring with half a hydrogen attached to the nitrogen are about 0.1370 nm as compared with an average 0.1325 nm for the nitrogens without hydrogens (outer ring). If titanyl is co-ordinated to the inner ring nitrogens, the same average 0.1370 nm distance for C–N bonds is observed as well as the 0.1325 nm average for the outer ring C–N bonds [2]. The hydrogens at the inner ring for β-H_2Pc are only partially occupied and the partial occupancy factor set to 0.5, which leads to a highly symmetric phthalocyanine molecule.

Two stacks of molecules are placed within the unit cell along the *b* dimension with the same absolute value of the setting angle of the planar molecule

TABLE V Torsion angles for β-H_2Pc

Atom 1	Atom 2	Atom 3	Atom 4	Angle (deg)
C8	N1	C1	C2	0.66 (0.18)
C1	N1	C8	N5	– 179.84 (0.15)
C1	N1	C8	C7	– 0.63 (0.18)
C16	N2	C9	N5	179.44 (0.16)
C16	N2	C9	C10	0.60 (0.18)
C9	N2	C16	N6	179.41 (0.15)
C9	N2	C16	C15	– 0.44 (0.17)
C9	N5	C8	N1	0.89 (0.26)
C9	N5	C8	C7	– 178.22 (0.15)
C8	N5	C9	N2	– 0.76 (0.27)
C8	N5	C9	C10	177.92 (0.15)
N1	C1	C2	C3	179.03 (0.17)
N1	C1	C2	C7	– 0.43 (0.18)
C1	C2	C3	C4	– 179.50 (0.17)
C7	C2	C3	C4	– 0.11 (0.25)
C1	C2	C7	C6	179.84 (0.14)
C1	C2	C7	C8	0.05 (0.24)
C3	C2	C7	C6	0.31 (0.26)
C3	C2	C7	C8	– 179.49 (0.15)
C2	C3	C4	C5	0.10 (0.29)
C3	C4	C5	C6	– 0.29 (0.28)
C4	C5	C6	C7	0.47 (0.27)
C5	C6	C7	C2	– 0.48 (0.25)
C5	C6	C7	C8	179.27 (0.17)
C2	C7	C8	N1	0.36 (0.19)
C2	C7	C8	N5	179.63 (0.14)
C6	C7	C8	N1	– 179.42 (0.17)
C6	C7	C8	N5	– 0.15 (0.29)
N2	C9	C10	C11	179.15 (0.17)
N2	C9	C10	C15	– 0.54 (0.18)
N5	C9	C10	C11	0.24 (0.28)
N5	C9	C10	C15	– 179.46 (0.15)
C9	C10	C11	C12	– 179.09 (0.17)
C15	C10	C11	C12	0.56 (0.25)
C9	C10	C15	C14	179.40 (0.15)
C9	C10	C15	C16	0.27 (0.19)
C11	C10	C15	C14	– 0.33 (0.25)
C11	C10	C15	C16	– 179.46 (0.15)
C10	C11	C12	C13	– 0.29 (0.27)
C11	C12	C13	C14	– 0.24 (0.30)
C12	C13	C14	C15	0.47 (0.27)
C13	C14	C15	C10	– 0.19 (0.25)
C13	C14	C15	C16	178.68 (0.17)
C10	C15	C16	N2	0.09 (0.20)
C10	C15	C16	N6	– 179.77 (0.15)
C14	C15	C16	N2	– 178.90 (0.18)
C14	C15	C16	N6	1.25 (0.29)

towards the b axis but opposite signs for the corner and centre stacks. The overlapping of the phthalocyanine molecules within one stack is depicted in Fig. 5 and is related to the photosensitivity as discussed in the literature [6].

3.2. X-H_2Pc

The Cartesian co-ordinates of the finally refined crystal structure from the neutron scattering data of X-H_2Pc are listed in Table VI. It should be noted that the molecules of the β-H_2Pc structure were kept fixed, that is, the bond lengths, the bond angles and the torsion angles are the ones listed in Tables III–V. A projection of the unit cell is depicted in Fig. 6. Because space group $Pna2_1$ has a true subcell in projection down the stacks (b-axis), which is half the original size ($a' = a/2$, $c' = c$), it is not surprising that the projection of the structure in [3] and the newly determined one agree in projections with two molecules present. For the structure refinement in projection the mostly non-overlapping reflections up to 0.49 nm determine to a large extent the goodness of the fit and the R value that is surprisingly low for both space groups in projection, $P2_1/c$ [3] and $Pna2_1$. The two structures are, however, quite different in three dimensions, since the setting angle of the plane in which a molecule is placed and the b-axis is positive for one stack and negative for the other when proceeding along the a-axis. This difference in the setting angle actually leads to a doubling of one dimension in the previously reported structure and to an orthorhombic unit cell. The β-polymorph, also with two molecules in

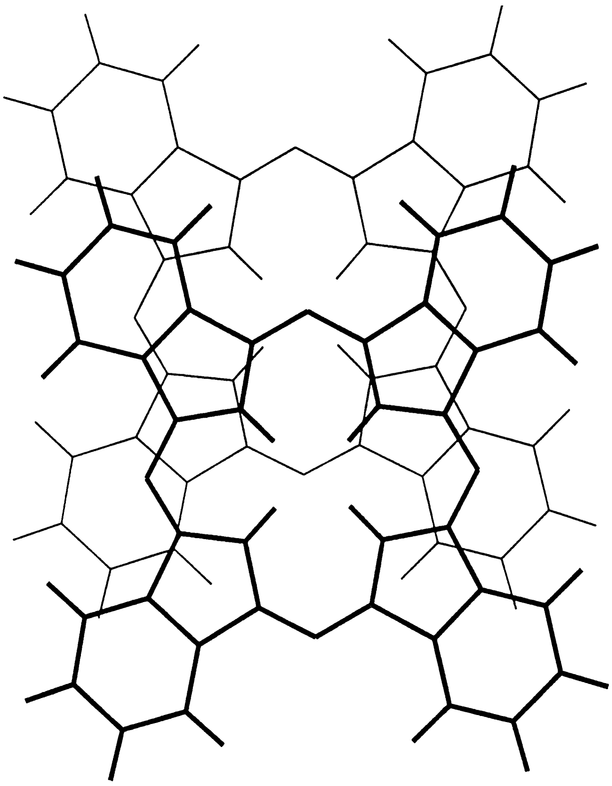

Figure 5 Projection of two molecules of β-H_2Pc in one stack onto the molecular plane.

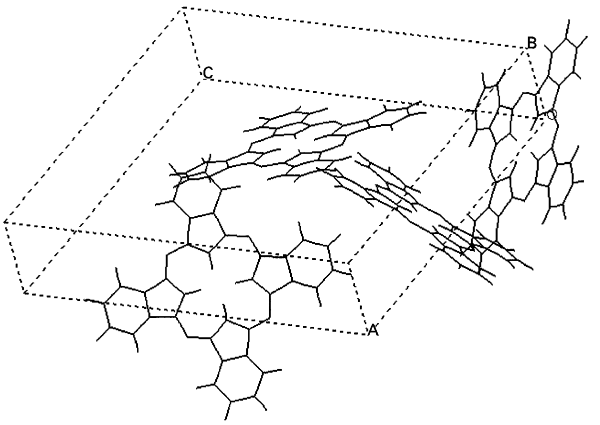

Figure 6 Representation of the packing of X-H_2Pc in space group $Pna2_1$. Position of the centre of symmetry of the asymmetric unit: (0.2625, 0.0, 0.0) nm.

TABLE VI Positional parameters for the atoms of the asymmetric unit and anisotropic overall B values for X-H_2Pc in space group $Pna2_1$ (Cartesian co-ordinates; symmetry related atoms are marked with*)

Atom	X (nm)	Y (nm)	Z (nm)
N1	0.1508	– 0.0059	0.1613
N2	0.1586	0.1491	– 0.0766
N5	– 0.0017	0.1738	0.1042
N6	0.2725	0.1859	– 0.2874
C1	0.1616	– 0.0908	0.2682
C2	0.0548	– 0.0620	0.3636
C3	0.0192	– 0.1183	0.4853
C4	– 0.0911	– 0.0658	0.5504
C5	– 0.1641	0.0395	0.4960
C6	– 0.1290	0.0966	0.3746
C7	– 0.0186	0.0435	0.3094
C8	0.0443	0.0772	0.1822
C9	0.0508	0.2048	– 0.0132
C10	– 0.0042	0.3081	– 0.0988
C11	– 0.1136	0.3926	– 0.0822
C12	– 0.1421	0.4808	– 0.1844
C13	– 0.0633	0.4849	– 0.2998
C14	0.0463	0.4020	– 0.3167
C15	0.0748	0.3128	– 0.2140
C16	0.1778	0.2110	– 0.1978
H3	0.0740	– 0.1978	0.5265
H4	– 0.1204	– 0.1061	0.6429
H5	– 0.2475	0.0764	0.5480
H6	– 0.1836	0.1766	0.3338
H11	– 0.1723	0.3894	0.0049
H12	– 0.2242	0.5458	– 0.1753
H13	– 0.0880	0.5528	– 0.3760
H14	0.1055	0.4064	– 0.4034
H1N	0.2079	– 0.0048	0.0853
H2N	0.2119	0.0784	– 0.0422
N1*	0.3742	0.0059	– 0.1613
N2*	0.3664	– 0.1491	0.0766
N5*	0.5267	– 0.1738	– 0.1042
N6*	0.2525	– 0.1859	0.2874
C1*	0.3634	0.0908	– 0.2682
C2*	0.4702	0.0620	– 0.3636
C3*	0.5058	0.1183	– 0.4853
C4*	0.6161	0.0658	– 0.5504
C5*	0.6891	– 0.0395	– 0.4960
C6*	0.6540	– 0.0966	– 0.3746
C7*	0.5436	– 0.0435	– 0.3094
C8*	0.4807	– 0.0772	– 0.1822
C9*	0.4742	– 0.2048	0.0132
C10*	0.5292	– 0.3081	0.0988
C11*	0.6386	– 0.3926	0.0822
C12*	0.6671	– 0.4808	0.1844
C13*	0.5883	– 0.4849	0.2998
C14*	0.4787	– 0.4020	0.3167
C15*	0.4502	– 0.3128	0.2140
C16*	0.3472	– 0.2110	0.1978
H3*	0.4510	0.1978	– 0.5265
H4*	0.6454	0.1061	– 0.6429
H5*	0.7725	– 0.0764	– 0.5480
H6*	0.7086	– 0.1766	– 0.3338
H11*	0.6973	– 0.3894	– 0.0049
H12*	0.7492	– 0.5458	0.1753
H13*	0.6130	– 0.5528	0.3760
H14*	0.4195	– 0.4064	0.4034
H1N*	0.3171	0.0048	– 0.0853
H2N*	0.3131	– 0.0784	0.0422

H1N, H2N, H1N* and H2N*: partial occupancy 0.5.
Overall B: $B_{11} = 0.035\ \mu m^2$, $B_{22} = 0.120\ \mu m^2$, $B_{33} = 0.034\ \mu m^2$.

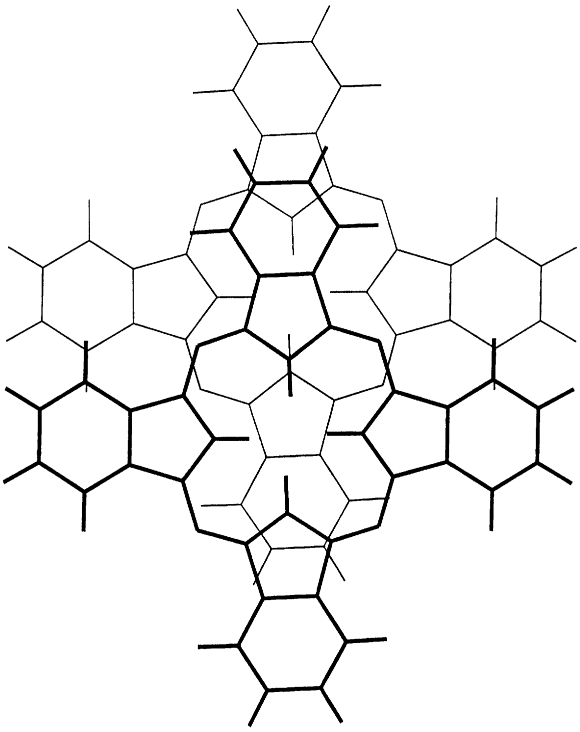

Figure 7 Projection of two adjacent molecules of X-H_2Pc in one stack onto the molecular plane.

the unit cell, differs greatly by the rotational position of the molecules within the stacks that then leads to a different overlap of the phthalocyanine molecules when projected onto the molecular plane (cf., Figs 5 and 7). Because the structures in projections for the previously published structure and the newly determined one are almost the same, the overlap has to agree also.

An anisotropic overall disorder factor, B, describing the average deviation of the mean atomic position from an ideal lattice (temperature motion and displacement by disorder) was found for the X-H_2Pc structure with higher values along the b-axis. Because B represents the mean squared deviation from the ideal lattice points, the average deviation (disorder) in the b-direction is about two times the deviation in a or c, respectively.

4. Conclusions

Comparing the two metal free phthalocyanines, β-H_2Pc and X-H_2Pc, the β-polymorph has a slightly higher density, $\rho = 1.45\ g\,cm^{-3}$, as compared with $1.43\ g\,cm^{-3}$ for X-H_2Pc calculated from the diffraction data, which suggests that β-H_2Pc is the more stable form.

From the diffraction data, it can also be concluded that β-H_2Pc possesses two, X-H_2Pc four stacks with different yet symmetry related setting angles in space for a single molecule within the unit cell. It is noteworthy that β-H_2Pc can be described with an overall isotropic temperature factor having no stacking faults with the consequence that the β-polymorph forms single crystals on a macroscopic scale. However, X-H_2Pc, which clearly shows stacking faults, substantiated by an anisotropic disorder (temperature) factor, crystallizes in microscopic single crystals only. This correlation between disorder and crystallite size is well known in the polymer crystal field. The influence of disorder and crystal size on the photosensitivity is not known at the present.

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