X-Form metal-free phthalocyanine: crystal structure determination using a combination of high-resolution X-ray powder diffraction and molecular modelling techniques

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A combination of high resolution X-ray diffraction and molecular modelling techniques have been used to determine (R_{wp} = 12.51%) the crystal structure of the X-form of metal-free phthalocyanine. It was found to crystallise in a bimolecular monoclinic unit cell (space group $P2_1/a$) with lattice parameters a = 10.63, b = 23.15, c = 4.89 Å, β = 95.98° in a 'herring-bone' molecular packing motif with a smaller angle (50°) than is found in the more stable β-polymorph (89°).

In this communication we demonstrate the utility of a novel methodology currently under development, which allows the crystallographic structures of organic molecular materials to be determined. This methodology can be used in the many instances when speciality materials of significant industrial importance, *e.g.* dyes, pigments and pharmaceuticals, cannot be treated with conventional single crystal techniques. Indeed, this was the case with the present example, the X-form of metal-free phthalocyanine (H_2Pc). Metal-free phthalocyanine is well known as a polymorphic material, with three established forms, the α-form,[1] the stable β-form[2] and the X-form. Given the high value of the least squares R-factor, 20%, for a previous determination[3] of the structure from powder diffraction data, together with improbable values for certain bond lengths and angles, it was considered worthwhile to re-examine the crystal structure of this material.

The general methodology applied here has been described elsewhere.[4,5] Here we describe details specific to the present example; a powdered crystalline sample of the X-form (H_2Pc). High-resolution (synchrotron) powder diffraction data were collected using a Debye–Scherrer scattering geometry on beamline 2.3 of the Synchrotron Radiation Source (SRS) at CCRL Daresbury Laboratory in the UK.[6] The incident beam wavelength was selected using a Ge(111) monochromator to be 1.5996 Å. Data were collected using an angular scanning range of 2θ from 5 to 55° at a step size of 1 mdeg and using a counting time of 4 s per point. Unit cell dimensions were determined from the first 20 reflections using the indexing programs DICVOL[7] and ITO.[8] The space group was determined by consideration of systematic extinction conditions. The systematic absences were consistent with the monoclinic space group $P2_1/a$. Consideration of the density and packing coefficient indicated a bimolecular cell (Z = 2).

A molecular model of the metal-free phthalocyanine was refined using the semi-empirical molecular orbital package MOPAC[9] with the AM1 method. In this calculation full symmetry was employed in the Z-matrix specification of bond lengths, angles and torsions. All possible orientations of the refined molecule in the unit cell, given the determined cell and space group, were systematically searched using a computer algorithm. Space group symmetry considerations imposed the constraint that the centre of coordinates of the asymmetric unit must lie at the origin of the cell. In this example therefore, it was necessary only to examine the three rotational degrees of freedom of the asymmetric unit. Good configurations were determined on the basis of a calculated lattice energy. The systematic search algorithm covered the rotational space of the asymmetric unit within an angular range of 0 to 180°, in three mutually orthogonal directions, with a step size of 2°. The search through a total of 729 000 configurations was completed in 4 h on a Silicon Graphics Indigo[2] workstation with R4400 processor. Lattice energies were determined using pairwise atom–atom summation, the force-field parameters of Momany *et al.*[10] and charges from the MOPAC calculations.

Table 1 Comparison of the crystal chemistry of the X- and β-polymorphs of metal-free phthalocyanine

Parameter	β-Form	X-Form (this determination)	X-Form (previous determination)
a/Å	19.85	10.63	21.40
b/Å	4.72	23.15	23.70
c/Å	14.80	4.89	4.90
β/°	122.28	95.98	30.4
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$
Z	2	2	2
V/(Å^3)	1172.3	1194.2	1251.6
Density/g cm^{-3}	1.46	1.43	1.36
Lattice energy/kcal mol^{-1}	−45.5	−43.6	+81.0
Packing coefficient	0.72	0.70	0.67

X-Ray power diffraction profiles were simulated for the best packing configurations obtained from the systematic search and compared with the experimental data. Using the refined scale factor as a quantitative ranking of the trial structures, the best trial structure was selected for final Rietveld refinement. In this case the trial structure with the most stable lattice energy (−41.9 kcal mol^{-1}) from the systematic search showed best agreement with the experimental data. The agreement was very satisfactory, and readily allowed a final Rietveld refinement to be undertaken. There were 15 independent parameters in the profile refinement model, the number of reflections in the measured angular range was 237. The refinement was undertaken using the program DBWS.[11] Given the requirement of keeping the number of parameters in the refinement model small, the only parameters relating to molecular structure in the refinement model were three independent bond lengths and two bond angles.

Table 1 gives the refined cell parameters of the X-form (and for comparison values, for the β-polymorph). The fractional coordinates of the asymmetric unit have been deposited at the

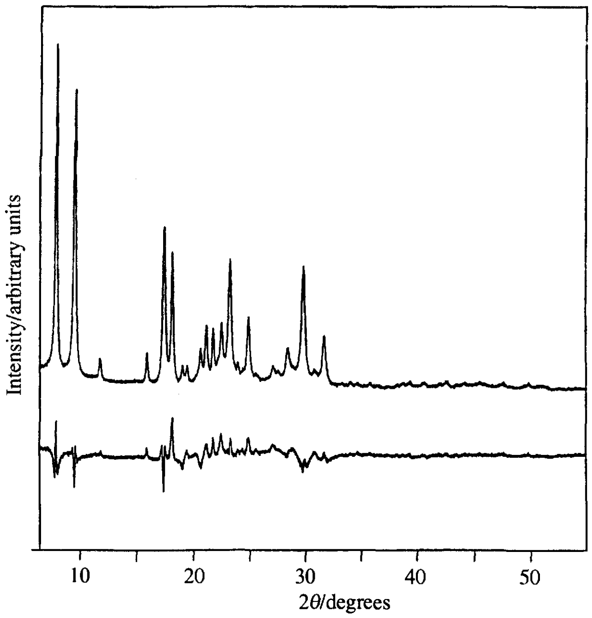

Fig. 1 X-Ray powder diffraction data and final Rietveld plot for X-form metal-free phthalocyanine

Cambridge Crystallographic Data Centre.† The powder data was considered insufficient in quantity to allow the reliable calculation of temperature factors. Fig. 1 shows the original powder data and final Rietveld difference plot after structure refinement. The present structure solution is substantially different to the previous determination and gives an improved least squares R-factor of 12.5%. Further, it is interesting to note that the calculated lattice energy of the structure, described in this communication, is -43.6 kcal mol^{-1} whereas that for the previously determined structure is $+81.0$ kcal mol^{-1}. These lattice energies clearly underline our concern over the previous determination. The β polymorph which is the more stable form[2] has a calculated lattice energy of -45.5 kcal mol^{-1}.

The high lattice energy, low density and anomalous bond lengths (C–N 1.06 Å, N–C 1.59 Å, C–C 1.59 Å) and angles calculated from the previous structure solution are of some concern. The packing arrangement from the previous determination manifests large voids around the molecular stacks along the c-axis. The packing in the new structure is more efficient giving a packing coefficient of 0.70, compared with 0.67. The stable β-form has a packing coefficient of 0.72. The most apparent structural difference between the X- and β-forms is in the angles, 50 and 89°, respectively, between the planes of the molecules which define the 'herring-bone' packing arrangement. This is illustrated in Fig. 2.

A novel methodology, currently under development, has been successfully applied to determine the crystal structure of the X-form (H_2–Pc). Comparison with a previous determination shows a much improved R-factor for the goodness of fit, and a calculated lattice energy in much better agreement with that of the stable β-form. The speed and reliability of the computer algorithm which performs a systematic search for trial structures has been demonstrated. This methodology is currently being applied to examples where molecular translation within the cell, and conformational flexibility are also present.

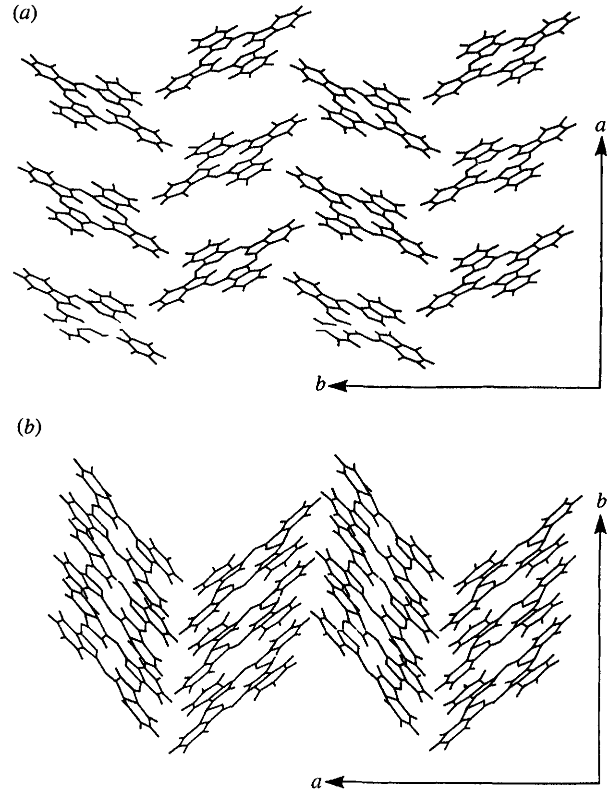

Fig. 2 Packing diagram illustrating the comparative crystal chemistry of (a) the X-form and (b) the β-form metal-free phthalocyanine

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