The Crystal Structure of Quinacridone: An Archetypal Pigment

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The crystal structure of γ-quinacridone is reported and the relationship between the γ- and γ′-polymorphs discussed.

Despite the commercial significance of non-azo organic pigments few full crystal structures of these materials have been reported.[1] By their very nature pigments are insoluble and solution growth methods therefore inappropriate. Vapour deposition, whilst of more value, rarely produces crystals of suitable quality for conventional X-ray structure determination. As a result, those important crystallographic features controlling the crystal chemistry of such materials have remained unknown. An example is provided by quinacridone for which full crystal data has not been published.

The first unambiguous synthesis route[2] for quinacridone was established in 1935. Despite the considerable commercial interest which followed[3,4] difficulty in growing suitable crystals has meant that the crystal structure for this archetypal pigment has not been reported. Indeed earlier crystallographic studies have been restricted to reporting only cell-parameter data, Table 1.[5,6] Quinacridone, however, is still a much studied and reported on material[7,8] and an understanding of the intermolecular forces at play and which give rise to such atypical properties (*i.e.* low solubility and high melting point) for an organic crystal remains uncertain. Such an understanding is vital to the systematic design of new and improved pigments.

Diffraction methods using synchrotron radiation (SR) for a variety of applications have been developed recently, and in particular the development of facilities for studying crystals too small for analysis with conventional sealed-source diffractometers. We report here an SR determination of the crystal structure of quinacridone and discuss the intermolecular interactions present in the crystal lattice. In addition we use this structural information to rationalise the apparent range of polymorphic forms which have been reported for quinacridone.

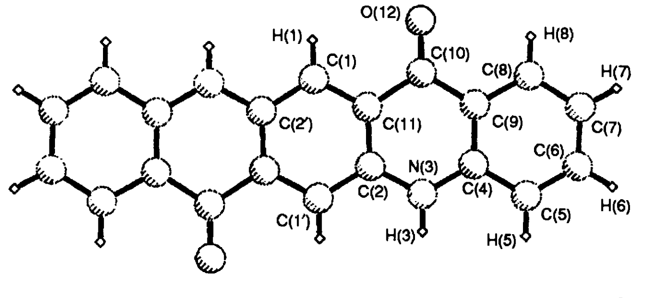

Fig. 1 PLUTO[12] plot for quinacridone with selected bond lengths (Å) and angles (°): C(11)–C(1) 1.406(7), C(11)–C(2) 1.403(7), C(11)–C(10) 1.489(8), C(9)–C(4) 1.408(8), C(9)–C(8) 1.412(9), C(9)–C(10) 1.454(8), N(3)–C(2) 1.368(7), N(3)–C(4) 1.378(7), C(1)–C(2′) 1.414(8), C(4)–C(5) 1.417(8), C(10)–O(12) 1.241(7), C(5)–C(6) 1.360(9), C(7)–C(8) 1.397(9), C(7)–C(6) 1.388(10), C(1)–C(11)–C(2) 120.5(5), C(1)–C(11)–C(10) 119.5(5), C(2)–C(11)–C(10) 119.9(5), C(4)–C(9)–C(8) 119.4(5), C(4)–C(9)–C(10) 120.3(5), C(8)–C(9)–C(10) 120.3(5), C(2)–N(3)–C(4) 121.6(4), N(3)–C(2)–C(11) 121.1(5), N(3)–C(2)–C(1′) 119.8(5), C(11)–C(2)–C(1′) 119.1(5), C(11)–C(1)–C(2′) 120.4(5), N(3)–C(4)–C(5) 118.6(5), N(3)–C(4)–C(9) 121.2(5), C(5)–C(4)–C(9) 120.2(5), O(12)–C(10)–C(9) 122.6(5), O(12)–C(10)–C(11) 121.6(5), C(9)–C(10)–C(11) 115.8(5), C(6)–C(5)–C(4) 118.7(5), C(8)–C(7)–C(6) 119.8(6), C(5)–C(6)–C(7) 122.5(6), C(7)–C(8)–C(9) 119.3(6)

A sample of quinacridone was heated in a sealed evacuated glass tube (*ca.* 10^{-3} Torr) at 420 °C. Small, red plate-like crystals deposited near the cooler surfaces. A crystal of dimensions 350 × 75 × 15 μm was selected and mounted on a single strand of glass wool (≈10 μm) attached to a stronger glass fibre. X-Ray data collection† was performed using an Enraf-Nonius area detector with the on-line version of the MADNES[9] software (implemented on a MicroVAX II) controlling the FAST diffractometer on Station 9.6 at the Daresbury Laboratory. Intensity data were accumulated on the area detector (crystal-detector distance 40.4 mm) with each 'frame' involving 0.2° of rotation in 15 s, for $\phi = 0$–200°. Merging yielded 913 unique reflections and direct methods[10] were used to generate a structure solution. Refinement was carried out using least squares analysis[11] to final $R = 0.1214$.

The molecular geometry and atomic numbering scheme for quinacridone are shown[12] in Fig. 1. The molecule is planar with no significant departure of the carbonyl groups from a molecular plane defined by all non-hydrogen atoms. The molecule adopts a herring-bone packing arrangement with individual stacks of quinacridone molecules rotated with respect to each other. Individual molecules are hydrogen-bonded through N–H···O short contacts to four adjacent molecules (Fig. 2) confirming the important contribution that hydrogen-bonding makes to the overall stability of the lattice[5–8] [The N–H···O separation distance of 1.94 Å in quinacridone is comparable to the corresponding intermolecular separation in the acridone crystal (1.92 Å)[13]]. This hydrogen-bonding appears to be primarily responsible for the overall orientation of the quinacridone molecules in the lattice and, hence, the packing arrangement and solid-state properties. Further lattice stabilisation results from π–π interactions between molecules within individual stacks.

This importance of hydrogen bonding and π–π interactions in influencing the crystal is apparent in the morphology of the crystals which result from vapour growth.[5] The plate-face

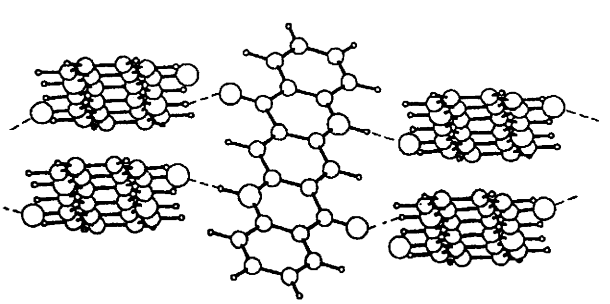

Fig. 2 Packing motif in quinacridone. Linkage of molecules *via* N–H···O hydrogen-bonds to four neighbours.

Table 1 Reported cell parameters for quinacridone obtained from single-crystal measurements

Source	*a*/Å	*b*/Å	*c*/Å	β/°
Koyama *et al.*[6]	13.79	3.89	13.44	100.5
Chung and Scott[5]	14.116(10)	3.885(3)	13.377(10)	107.22(8)
This work	13.761(6)	3.895(3)	13.439(4)	100.33(4)

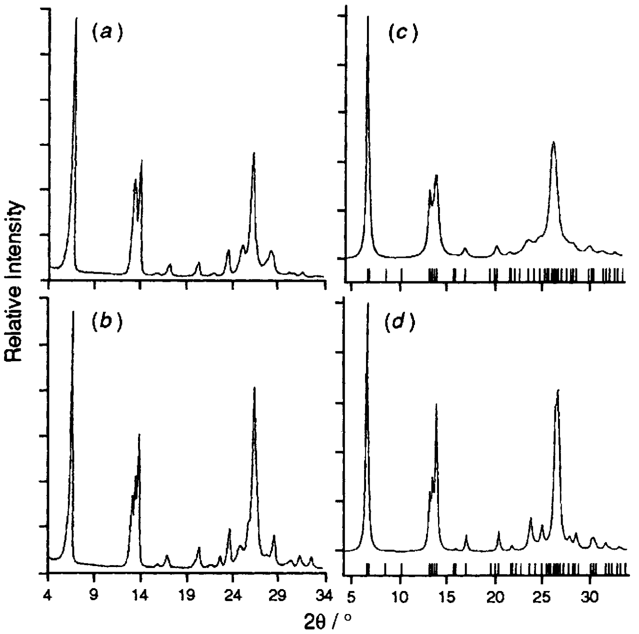

Fig. 3 Experimental X-ray powder patterns for (*a*) γ- and (*b*) γ′-forms of quinacridone. The simulated patterns using two different crystal morphologies are shown in (*c*) 300 × 50 × 125 Å and (*d*) 350 × 150 × 350 Å. Both patterns were simulated using Cerius Version 3.0.2. software and using the atomic coordinates reported here.

[indexed through optical goniometry as the (100)] involves only molecular edge-on interactions and is the prominent face. Directions in which π–π and N–H···O interactions act (*i.e.* in the direction of the *b* and *c* axes respectively) lead to rapid growth rates. These anisotropic growth rates clearly result in the plate-like crystals.[14] Furthermore, as grown, quinacridone appears as aggregates which readily shear. During handling, therefore, considerable mosaic spread may result giving rise to inaccurate unit-cell dimensions. That the unit cell determined by Chung and Scott[5] may belong to a different quinacridone polymorph is, on the basis of the powder X-ray data described below, considered unlikely.

Although polymorphism frequently occurs in organic materials, unambiguous identification based on powder X-ray data is difficult. In the case of quinacridone at least seven polymorphic forms[15–21] have been reported on the basis of powder X-ray data although only three, *viz.* α,[15] β[16] and γ[17] are widely accepted. The greatest doubt exists over the existence of an additional γ-like phase frequently designated γ′.[22] Evidence for this particular phase is based on two subtle variations in experimental powder diffraction patterns; (*i*) the γ′ phase gives rise to a triplet at approximate *d* spacing 6.5 Å, whereas the γ phase has a doublet and (*ii*) γ′ has a reversal of the relative peak intensities at 3.56 Å and 3.74 Å observed for the γ form.

The availabilty of the full structural data reported here allows the possible existence of the two (γ and γ′) polymorphs to be addressed. The intensities of reflections in X-ray powder diffraction patterns are known to be dependent upon a number of effects, including in particular crystallite size and crystal morphology. In Fig. 3 we show that it is possible using the crystal coordinates and by modifying the average crystallite size[23] to reproduce the diffraction pattern of both the γ and γ′ phases. As a result we suggest that there is in fact only one γ phase with the differences in powder pattern being simply related to the crystallite shape and size.

At present, we are pursuing a more quantitative analysis of the packing energy of quinacridone and of other pigments with the intention of further rationalising the important features controlling the solid state characteristics of organic pigments.

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Footnote

† *Crystal data* For $C_{20}H_{12}N_2O_2$: $M = 309.98$, monoclinic, space group $P2_1/c$; at 293 K, $a = 13.761(6)$, $b = 3.895(3)$, $c = 13.439(4)$ Å, $\beta = 100.33(4)°$, $V = 708.64$ Å^3, $Z = 2$, $\mu = 0.096$ mm^{-1}, $F(000) = 324.00$, $D_c = 1.464$ g cm^{-3}. Intensity data were collected on Station 9.6 ($\lambda = 0.895$ Å), EPSRC Daresbury Laboratory, Warrington, Cheshire. Total number of unique reflections 913, of which 775 had $I > 4\sigma(I)$. The structure was solved by direct methods (SHELXS-84) and was refined by full-matrix least-squares calculations to $R = 0.1214$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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