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Key indicators

2,6-Dihydroxyanthraquinone: an isomer of the well known alizarin dye

The structure of anthraflavic acid (2,6-dihydroxyanthraquinone), $C_{14}H_8O_4$, an isomer of the alizarin dye, adopts a planar conformation, with crystallographic *mm* symmetry. Its crystal packing, which can be described as superimposed sheets of molecules (like a graphite structure), is very different from that of alizarin, which contains a herringbone stacking of molecules.

Comment

Carbonyl dyes owe their success to their ability to provide a wide range of colors covering the entire visible spectrum. In particular, 9,10-anthraquinone derivatives in which the central ring bearing two carbonyl groups is fused to two fully aromatic six-membered rings can give rise to a complete range of shades (especially in the green–blue region), depending on the nature and relative position(s) of the auxochromic group(s) substituting H atom(s) on the outer rings (Labhart, 1957; Zollinger, 2003).

(I)
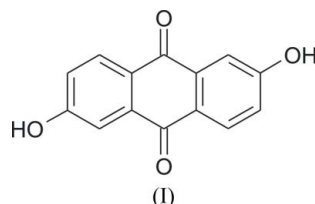
This work is the first step in the study of the effect of the surroundings in terms of crystal packing. Amongst the positional isomers [Cambridge Structural Database (CSD; Version 5.27, November 2005; Allen, 2002) refcodes DHANTQ01, DHXANT and DHANQU] of the well known alizarine dye
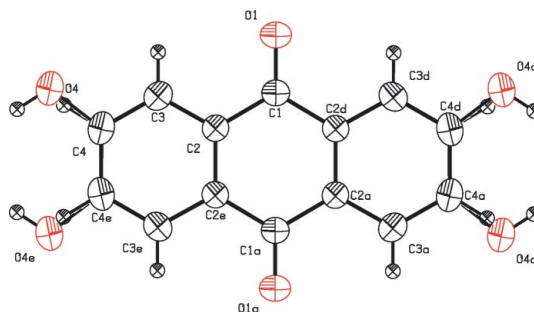

Figure 1
The molecular structure of 2,6-dihydroxyanthraquinone. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown. [Symmetry codes: (a) $1 - x, -y, z$; (d) $\frac{1}{2} + y, -\frac{1}{2} + x, -z$; (e) $\frac{1}{2} - y, \frac{1}{2} - x, -z$.]
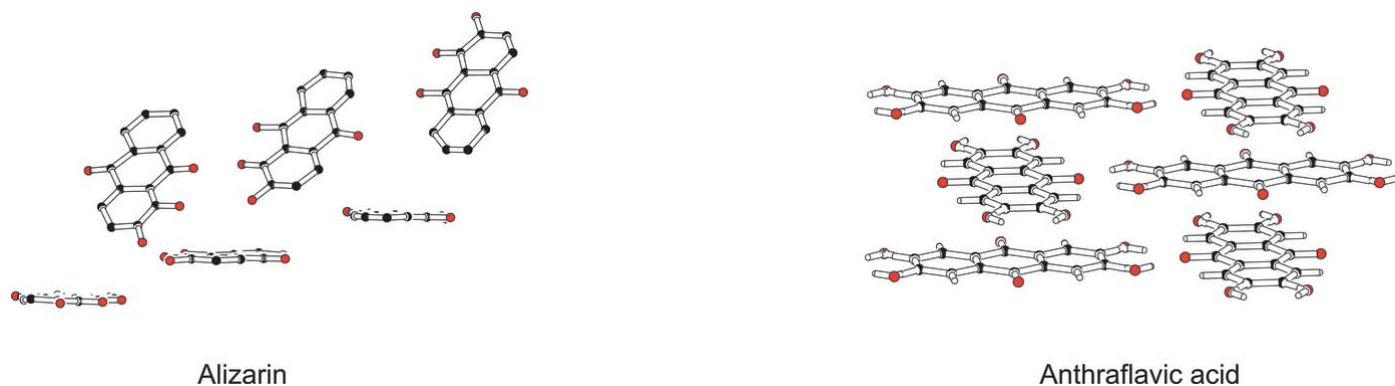
Figure 2
Comparison of the crystal packing of alizarin and anthraflavic acid.

(Guilhem, 1966; CSD refcode DHYANT, space group Pa), the crystal structure of anthraflavic acid (2,6-dihydroxy-anthraquinone) was still missing.

The title compound, (I), crystallized in the space group $I4/mcm$, which is not very common for organic or metal-organic molecules (approximately 20 structures reported in the CSD). As a result of this high symmetry, mm for the molecule, the complete structure was solved and refined using only six atoms, *viz*. C1, C2, C3, C4, O1, O4. All six atoms lie in the ab plane, leading to a planar compound. After the first round of refinement, we obtained a model with a hydroxyl group on C4 that is reproduced by symmetry at C4a, C4d and C4e (Fig. 1). In order to account for the chemical structure, alternative occupancies of a hydroxyl and an H atom were introduced in the model; occupancy of each of these was set to 0.5. In this way, the structure has alternatively an OH group or an H atom on C4. So, in the final structure, when C4 and C4a bear an OH group, positions C4d and C4e are linked to an H atom and *vice versa*. A hydrogen bond is established between the carbonyl oxygen (O1) and the hydrogen (H4) of a hydroxyl unit of another molecule (Table 1). The molecules form a cage-like tetramer. A void is present in the centre of this tetrameric assembly. The crystal packing can be described as multiple layers of molecules along the c axis. The distance between adjacent layers is 3.3 Å, corresponding to a graphite-like structure. This is an important difference compared to the packing of the alizarin dye which contains a herringbone stacking of molecules (Fig. 2).

Using *GAUSSIAN03* (Frisch *et al.*, 2004), the λ_{max} of absorption of alizarin and anthraflavic acid have been computed at the PCM(EtOH)-TD-B3LYP/6–31 $G(d,p)$// B3LYP/6–31 $G(d,p)$ level of approximation, following our previous theoretical investigation of the visible spectra of anthraquinones (Jacquemin *et al.*, 2004). The predicted values, 439 and 352 nm, respectively, are in perfect agreement with available experimental data in the same solvent (ethanol) (435 and 349 nm; Weast, 1970). We are currently using theoretical tools to obtain the UV–vis spectra of solid alizarin and anthraflavic acid. We propose that the visible spectra should be different because of the variations in the crystal packing of the two compounds.

Experimental

The title compound was purchased from Sigma–Aldrich. Yellow thin needles of the compound were obtained by slow evaporation of a methyl acetate–acetone (1:1) solution.

Crystal data

$C_{14}H_8O_4$	$D_x = 1.284$ Mg m^{-3}
$M_r = 240.20$	Cu $K\alpha$ radiation
Tetragonal, $I4/mcm$	$\mu = 0.80$ mm^{-1}
$a = 13.640$ (4) Å	$T = 293$ (2) K
$c = 6.678$ (3) Å	Thin needle, yellow
$V = 1242.4$ (8) Å^3	$0.50 \times 0.19 \times 0.15$ mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	375 independent reflections
$\omega/2\theta$ scans	346 reflections with $I > 2\sigma(I)$
Absorption correction: analytical	$R_{int} = 0.022$
(Alcock, 1970)	$\theta_{max} = 75.0°$
$T_{min} = 0.691$, $T_{max} = 0.890$	3 standard reflections
702 measured reflections	frequency: 60 min
	intensity decay: 11.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1314P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 0.1721P]$
$wR(F^2) = 0.188$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.20$	$(\Delta/\sigma)_{max} < 0.001$
375 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
35 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4···O1	0.82	1.86	2.68	178

All H atoms were fixed at localized positions, except for the H atom on O4, which was found in a difference Fourier map and refined.

Data collection: *CAD-4/MACH3* (Nonius, 2000); cell refinement: *CAD-4/MACH3*; data reduction: *HELENA* (Spek, 1997); program(s)

used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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