

Disodium 2,5-bis(phenylamino)-terephthalate decahydrate, an intermediate in the industrial synthesis of quinacridone pigments

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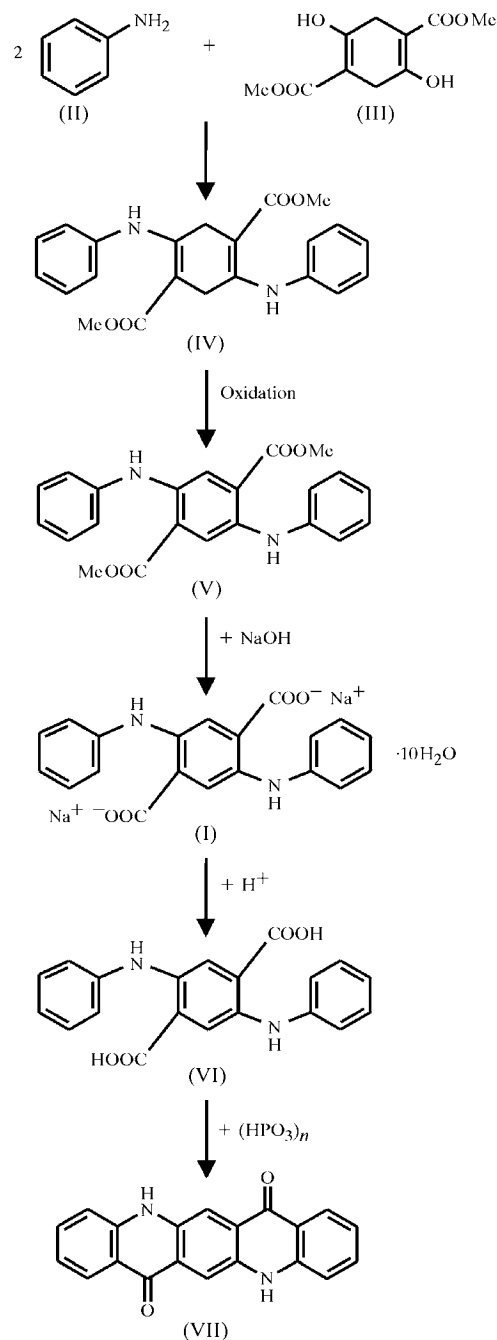
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The title compound, $2\text{Na}^+ \cdot \text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_4^{2-} \cdot 10\text{H}_2\text{O}$, is an intermediate in the industrial synthesis of red and violet quinacridone pigments. The structure is remarkable for two reasons. First, one of the Na^+ ions is surrounded octahedrally by five water molecules and a phenyl group, although the crystal contains many more water molecules than are required for complete coordination of both Na^+ ions with six water molecules each. Secondly, although the anion has almost exact molecular inversion symmetry, it is positioned on a general position; this is one of the very few exceptions to the observation of Kitajgorodskij [*Advances in Structure Research by Diffraction Methods – Fortschritte der Strukturforchung mit Beugungsmethoden* (1970), Vol. 3, pp. 173–247] that molecules with inversion centres always lie on crystallographic inversion centres.

Comment

Quinacridone, (VII) (see scheme), worldwide registered as C.I. Pigment Violet 19, is the most important pigment for red–violet shades (Herbst & Hunger, 2004). The pigment is produced at a rate of several thousand tons per year and the annual sales are more than 100 million euros. It is used for automotive finishes, powder coatings, paints, plastics and high-grade printing inks. The most common industrial synthetic route starts with condensation of aniline (II) and succinylsuccinic ester (dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate), (III), followed by oxidation and alkali treatment, yielding the intermediate disodium 2,5-bis(phenylamino)terephthalate decahydrate, (I). This intermediate is converted to the corresponding acid (VI) and treated with molten polyphosphoric acid to yield the quinacridone (VII) in the α , β or γ phase, depending on the synthetic conditions (Urban *et al.*, 1998, 2000; Herbst & Hunger, 2004). The violet β phase and the red γ phase are used commercially as pigments.

Quinacridone has been known since 1935 (Liebermann *et al.*, 1935) and industrially produced since 1958 (Reeve & Botti,



1958). The crystal structures of β - and γ -quinacridone are known (Paulus *et al.*, 1989; Potts *et al.*, 1994), but despite their industrial relevance, not one crystal structure of an intermediate has been determined hitherto [Cambridge Structural Database (CSD); Version 5.26 of November 2004, plus three updates; Allen, 2002]. We report here the crystal structure of the intermediate (I), also called ‘anilic acid sodium salt’. The molecular structure is shown in Fig. 1.

The crystal structure consists of 2,5-bis(phenylamino)terephthalate dianions and sodium cations, which are coordinated by water molecules (see Fig. 2). There is no direct sodium–carboxylate contact.

The anion exhibits two intramolecular hydrogen bonds from the NH groups to the carboxylate moieties. The whole diaminoterephthalate unit is almost planar (the r.m.s. deviation for all non-H atoms is 0.0706 Å). In contrast, the two phenyl rings are twisted against the central terephthalate unit by 58.44 (6) and 51.08 (6)° for the C21–C26 and C51–C56 rings, respectively. For the final synthetic step, *i.e.* the ring closure, the intramolecular hydrogen bonds have to be broken and the aniline moiety must be rotated by approximately 150° (Table 1). Under the applied synthetic conditions (molten polyphosphoric acid at 373–473 K) these rotations are easily achieved.

The anion adopts almost exact inversion symmetry. According to the observation of Kitajgorodskij (1970), all molecules with molecular inversion symmetry maintain this symmetry in the crystal, *i.e.* they are always positioned on crystallographic inversion centres. Hence, the 2,5-bis(phenyl-amino)terephthalate dianions should be on an inversion

centre, and there should be either one Na atom on a general position or, for example, two Na atoms on inversion centres. Astonishingly, in the present structure the anion is not situated on an inversion centre but on a general position. This is one of the very few exceptions to Kitajgorodskij's rule.

A thorough search of the CSD shows that 99% of all molecules with point group $\bar{1}$ are actually situated on crystallographic inversion centres (Pidcock *et al.*, 2003). If the molecules have even higher symmetry, *e.g.* $2/m$, then the occupancy of $\bar{1}$ drops to 97% as other special positions (*e.g.* 2 or m) are possible. The remaining 3% may include some structures with overlooked symmetry, but there are a few accurately determined structures where a molecule with

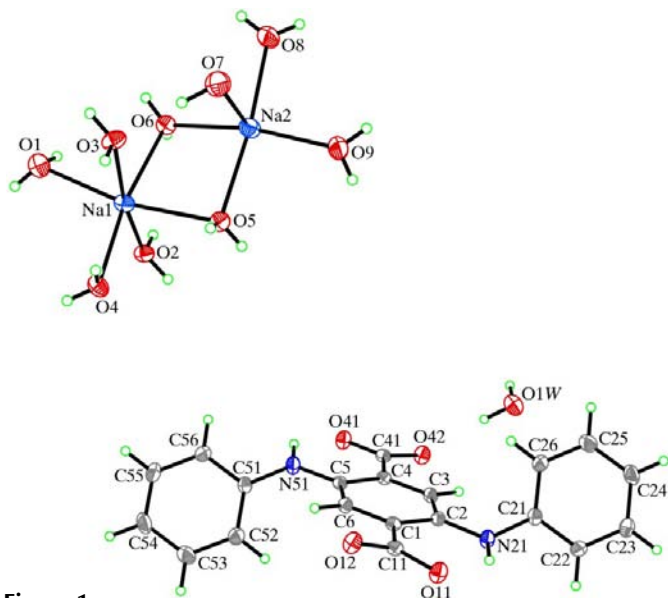


Figure 1

A perspective view of the title compound, with the atom numbering; displacement ellipsoids are shown at the 50% probability level. One of the H atoms bonded to atom O7 is not shown because it could not be clearly located and was therefore omitted from the refinement.

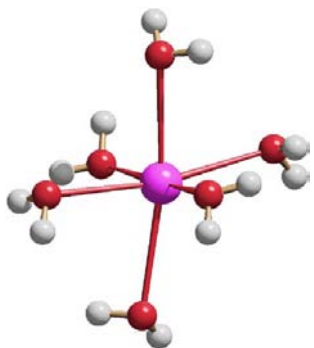


Figure 2

The coordination of Na1.

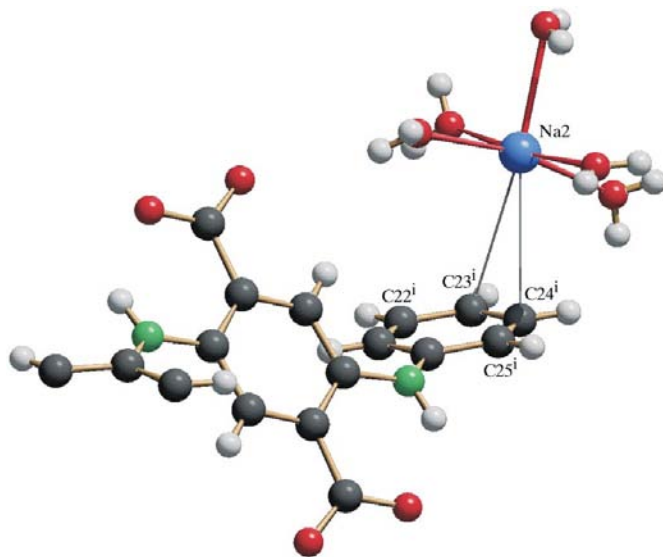


Figure 3

The coordination of Na2 [$\text{Na}2 \cdots \text{C}21^i = 4.7320(19) \text{ \AA}$, $\text{Na}2 \cdots \text{C}22^i = 4.072(2) \text{ \AA}$, $\text{Na}2 \cdots \text{C}23^i = 3.240(3) \text{ \AA}$, $\text{Na}2 \cdots \text{C}24^i = 3.162(2) \text{ \AA}$, $\text{Na}2 \cdots \text{C}25^i = 3.943(2) \text{ \AA}$, $\text{Na} \cdots \text{C}26^i = 4.654(2) \text{ \AA}$ and $\text{Na}2 \cdots \text{C}g^i = 3.765 \text{ \AA}$; symmetry code: (i) $-x, -y + 1, -z + 1$; Cg is the centroid of the C21–C26 ring].

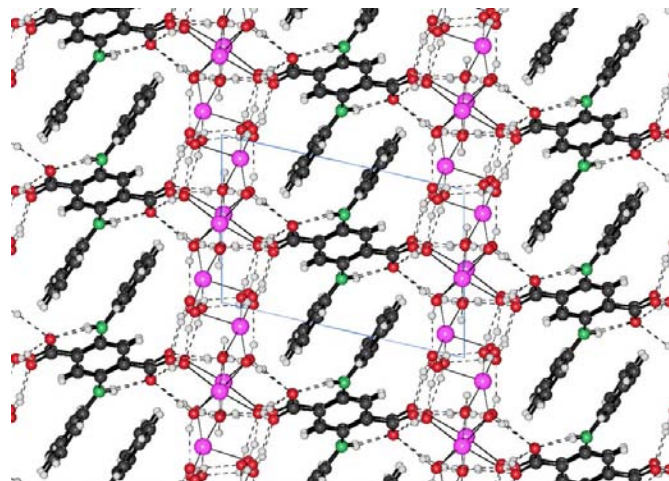


Figure 4

A projection of the layer structure of (I). The view direction is [010], with [100] vertical.

inversion symmetry is definitely situated on a general position, e.g. 1,5-dimethylnaphthalene ($P2_1/c$, $Z = 4$, $Z' = 1$; Beintema, 1965; Ferraris *et al.*, 1972; Wilson, 1997) and 2,2'-diaminodibenzyl ($P2_12_12_1$, $Z = 4$, $Z' = 1$; Narasegowda *et al.*, 2005). In these cases, the intramolecular inversion centre is only a local symmetry element, not a crystallographic one; this situation is comparable to the case of an asymmetric unit containing two crystallographically independent molecules, which are connected only by a local symmetry operation.

In the crystal structure of (I) we carefully checked that there was no erroneously missed crystallographic symmetry. A further indication is the existence of two symmetrically and chemically inequivalent sodium cations; atom Na1 is coordinated octahedrally by six water molecules (Fig. 2), whereas atom Na2 is octahedrally surrounded by five water molecules and a phenyl ring at a longer distance, which is bound only by van der Waals forces (Fig. 3). Sodium-phenyl contacts are also known for other compounds; these compounds contain either no water or only one water molecule per Na^+ ion (e.g. Hu *et al.*, 2002). It is very surprising that in compound (I) the Na2 atom prefers the neighbourhood of a phenyl group instead of being surrounded by water molecules only. Compound (I) is a decahydrate and contains many more water molecules than necessary for a complete coordination of both Na^+ ions; there is even one water molecule not bonded to any Na atoms. The reason for this unexpected coordination of Na2 remains obscure.

The structure is a double-layered structure (Fig. 4). The non-polar layer is formed by the phenyl rings; the polar layer contains the cations, the water molecules and the carboxy groups. The water molecules show a variety of coordination modes. Seven water molecules are coordinated to just one Na atom, two water molecules are shared between the sodium ions, and the tenth water molecule is not directly bound to any cation. Two (O2 and O3) of the nine water molecules that are coordinated to the Na cations bridge two anions *via* hydrogen bonds, four (O1, O5, O6 and O8) form hydrogen bonds between an anion and a water molecule, atom O4 is hydrogen bonded to the anion and to the water molecule that is not bonded to a Na atom, atom O7 forms hydrogen bonds to two Na-coordinating water molecules, and atom O9 is hydrogen bonded to a water molecule coordinating a sodium cation and the water molecule that is not bonded to a sodium cation. The water molecule (O1W) that is not coordinating a sodium cation forms hydrogen bonds to an anion and an Na-coordinating water molecule (Table 1).

Experimental

Industrially produced 2,5-bis(phenylamino)terephthalic acid ('anilic acid'), (VI), from the quinacridone plant of Clariant GmbH at Frankfurt-Höchst, was converted into the sodium salt (I) by stirring anilic acid (50 g) in a solution of NaHCO_3 (50 g) and water (450 ml) for 2 h. The mixture was filtered through a 20 μ filter to remove all particles. The solution was allowed to stand at room temperature in an open one-litre Erlenmeyer flask for several weeks. The resulting small pale-brown crystals were isolated from the solution and dried carefully with tissue paper.

Crystal data

$2\text{Na}^+\cdot\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_4^{2-}\cdot 10\text{H}_2\text{O}$
 $M_r = 572.47$
 Triclinic, $P\bar{1}$
 $a = 8.7638$ (7) Å
 $b = 12.4371$ (10) Å
 $c = 13.5720$ (11) Å
 $\alpha = 110.550$ (6)°
 $\beta = 97.483$ (7)°
 $\gamma = 101.857$ (6)°
 $V = 1322.14$ (19) Å³

$Z = 2$
 $D_x = 1.438$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 21410 reflections
 $\theta = 3.6$ – 27.2 °
 $\mu = 0.15$ mm⁻¹
 $T = 173$ (2) K
 Block, brown
 $0.19 \times 0.11 \times 0.09$ mm

Data collection

Stoe IPDS-II two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
 $T_{\min} = 0.973$, $T_{\max} = 0.981$
 21410 measured reflections

5789 independent reflections
 4837 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.078$
 $\theta_{\max} = 27.2$ °
 $h = -11 \rightarrow 11$
 $k = -15 \rightarrow 15$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.141$
 $S = 1.06$
 5789 reflections
 427 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2 + 0.5265P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1A···O12 ^x	0.85 (1)	2.01 (1)	2.8328 (18)	165 (3)
O1–H1B···O8 ⁱⁱ	0.84 (1)	2.61 (2)	3.130 (2)	121 (2)
O2–H2A···O42 ⁱⁱⁱ	0.85 (2)	1.99 (1)	2.8275 (18)	168 (3)
O2–H2B···O11 ^x	0.84 (1)	1.95 (1)	2.7740 (18)	168 (2)
O3–H3A···O12 ^{iv}	0.84 (2)	1.93 (1)	2.7632 (18)	171 (2)
O3–H3B···O41 ^v	0.84 (1)	1.88 (1)	2.7123 (18)	170 (2)
O4–H4A···O41 ^v	0.85 (1)	2.01 (1)	2.8522 (19)	178 (3)
O4–H4B···O1W ^{vi}	0.85 (1)	2.01 (1)	2.824 (2)	163 (2)
O5–H5A···O42 ^v	0.85 (1)	2.05 (1)	2.8895 (18)	170 (2)
O5–H5B···O4 ^v	0.84 (2)	2.16 (1)	2.9889 (19)	169 (2)
O6–H6A···O11 ^x	0.84 (1)	2.01 (1)	2.8513 (18)	172 (3)
O6–H6B···O1 ^{vii}	0.84 (3)	2.17 (1)	3.014 (2)	178 (2)
O7–H7B···O3	0.84 (1)	1.91 (1)	2.741 (2)	168 (3)
O8–H8A···O7 ^{viii}	0.85 (3)	2.15 (2)	2.925 (2)	154 (3)
O8–H8B···O12 ^{ix}	0.84 (1)	2.04 (1)	2.845 (2)	161 (3)
O9–H9A···O1W ⁱ	0.85 (4)	2.03 (2)	2.826 (2)	155 (4)
O9–H9B···O2 ^{xi}	0.85 (1)	1.98 (1)	2.8015 (19)	164 (3)
O1W–H1WA···O42	0.85 (1)	2.07 (1)	2.9059 (19)	166 (3)
O1W–H1WB···O9 ^{xii}	0.84 (3)	2.05 (2)	2.858 (2)	159 (4)
N21–H21···O11	0.91 (3)	2.03 (3)	2.7176 (19)	132 (2)
N51–H51···O41	0.90 (3)	2.03 (3)	2.6950 (19)	130 (2)

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 1, -z + 2$; (v) $x, y, z + 1$; (vi) $x + 1, y, z + 1$; (vii) $-x + 1, -y, -z + 2$; (viii) $-x, -y, -z + 2$; (ix) $x - 1, y - 1, z$; (x) $x, y - 1, z$; (xi) $x - 1, y, z$; (xii) $x, y, z - 1$.

All H atoms were located in a difference map. Those bonded to C atoms were refined with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model, with C–H distances of 0.95 Å. H atoms bonded to N atoms were refined isotropically. H atoms bonded to O atoms were refined with restraints of 0.84 (1) Å for O–H and 1.40 (1) Å for H···H distances. One of the H atoms bonded to atom O7 could not be clearly located and was omitted from the refinement.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991) and *SCHAKAL* (Keller, 1980); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1425). Services for accessing these data are described at the back of the journal.

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