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Anilic acid dimethylformamide disolvate

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Key indicators

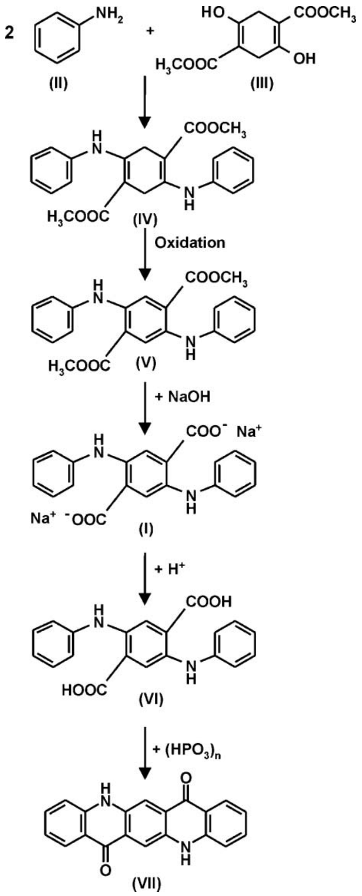
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.124
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Anilic acid [or 2,5-bis(phenylamino)terephthalic acid], $C_{20}H_{16}N_2O_4$, is an intermediate in the industrial synthesis of quinacridone pigments. Single crystals were grown from dimethylformamide (DMF), yielding a solvate with two molecules of DMF, $C_{20}H_{16}N_2O_4 \cdot 2C_3H_7NO$. There are two half-molecules of anilic acid in the asymmetric unit; each molecule is located on a centre of inversion and forms hydrogen bonds to two dimethylformamide molecules.

Comment

The most important pigment for red–violet shades is quinacridone (VII), which is worldwide registered as 'C. I. Pigment Violet 19′ (Herbst & Hunger, 2004). It is used for automotive finishes, powder coatings, paints, plastics and high-grade printing inks. The most common industrial synthetic route is shown in the reaction scheme.



The structure of the intermediate disodium aniloate (I) as the decahydrate has recently been published (Schmidt *et al.*,

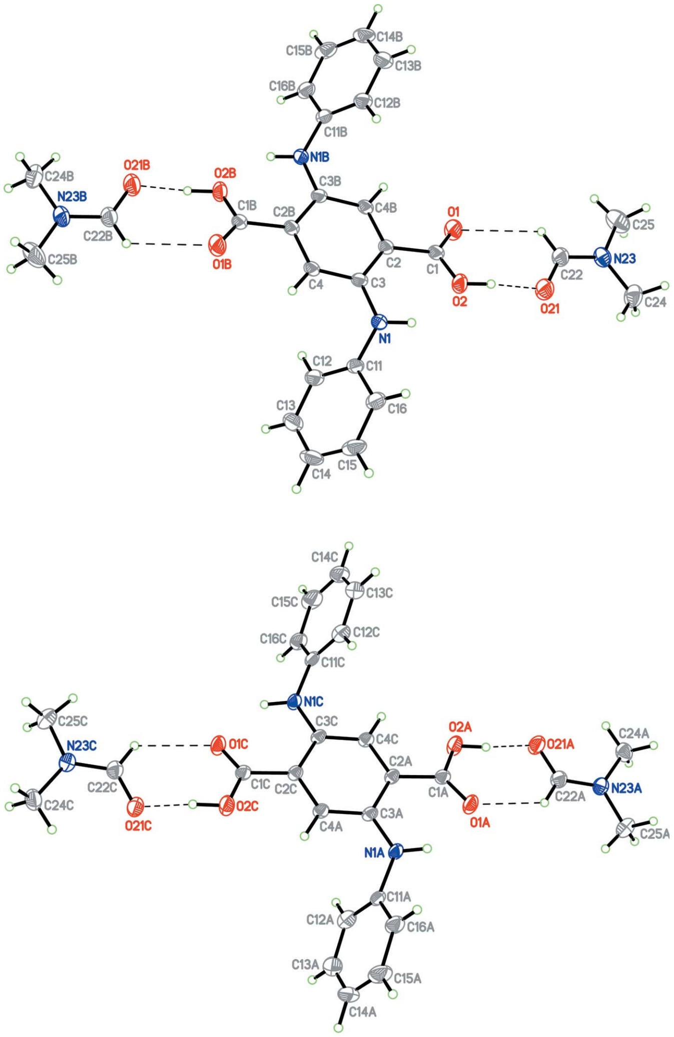


Figure 1

The structures of the two independent molecules together with their hydrogen-bonded solvent molecules. Atoms with the suffix *B* were generated by the symmetry operator $(-x, -y, 1 - z)$, while those with the suffix *C* were generated by the symmetry operator $(-x, 1 - y, 2 - z)$.

2006). The corresponding acid, or 2,5-bis(phenylamino)-terephthalic acid, is industrially called 'anilic acid'; it is produced in an amount of several thousand tons per year. One of the largest producers is Clariant. We report here the crystal structure of a dimethylformamide (DMF) solvate of this acid, (VI)·2DMF. For the crystallization, we used industrial anilic acid from the Clariant quinacridone plant in Frankfurt–Höchst (see below).

A perspective view of the title compound is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.27, November 2005 plus three updates; *MOGUL* Version 1.1; Allen, 2002). Each molecule of anilic acid is located on a centre of inversion. The dihedral angles between the central benzene ring and phenyl rings are 47.95 (5) and 59.09 (6)°. The carboxyl groups are twisted out of the central benzene plane by 17.12 (13) and 11.1 (2)°. The carboxyl groups form hydrogen bonds to DMF molecules (Table 1). The assemblies of one anilic acid and two DMF molecules are packed by van der Waals interactions.

Experimental

Anilic acid (10 g) was stirred with DMF (200 ml) for 2 h. The resulting solution was filtered over a 20 µm filter to remove all particles. The solution was kept in a open 200 ml Erlenmeyer flask at room temperature for several weeks allowing the anilic acid to crystallize slowly. Bright-orange crystals of anilic acid DMF solvate with a diameter of 1–2 mm were formed. The crystals were separated by filtration, washed with DMF and dried in a nitrogen flow.

Crystal data

$C_{20}H_{16}N_2O_4 \cdot 2C_3H_7NO$
$M_r = 494.54$
Triclinic, $P\overline{1}$
$a = 8.9875$ (8) Å
$b = 10.0220$ (8) Å
$c = 15.2076$ (12) Å
$\alpha = 83.088$ (6)°
$\beta = 74.144$ (6)°
$\gamma = 82.788$ (6)°
$V = 1301.92$ (19) Å^3
$Z = 2$
$D_x = 1.262$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 173$ (2) K
Block, orange
0.44 × 0.42 × 0.39 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: none
16656 measured reflections
4849 independent reflections
4385 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\rm max} = 25.6°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.124$
$S = 1.04$
4849 reflections
345 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.4015P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.54$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.39$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O21	0.93 (3)	1.60 (3)	2.5268 (14)	174 (3)
C22—H22···O1	0.95	2.59	3.2524 (18)	127
N1—H1···O2	0.902 (19)	2.006 (18)	2.6805 (15)	130.5 (16)
O2*A*—H2*A*···O21*A*	0.95 (3)	1.60 (3)	2.5432 (14)	173 (2)
C22*A*—H22*A*···O2*A*	0.95	3.14	3.2750 (17)	90
N1*A*—H1*A*···O1*A*	0.889 (19)	1.984 (19)	2.7049 (15)	137.2 (16)
C4—H4···O1$^{\rm i}$	0.95	2.44	2.7856 (16)	101
C4*A*—H4*A*···O2*A*$^{\rm ii}$	0.95	2.35	2.7003 (16)	102
C14—H14···O2*A*$^{\rm iii}$	0.95	2.52	3.3574 (18)	146
C14*A*—H14*A*···O1$^{\rm iv}$	0.95	2.58	3.469 (2)	157
C24—H24*A*···O21	0.98	2.34	2.7517 (19)	105
C24*A*—H24*D*···O21*A*	0.98	2.36	2.7824 (17)	105

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x, -y + 1, -z + 2$; (iii) $x + 1, y - 1, z - 1$; (iv) $x + 1, y, z$.

H atoms were located in a difference map, but those bonded to carbon were refined with fixed individual displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}$(methyl C)], using a riding model, with C—H = 0.95 and 0.98 Å for Csp^2 and methyl groups, respectively. The methyl groups were allowed to rotate but not to tip. H atoms bonded to N and O atoms were freely refined.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in

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SHELXTL-Plus (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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