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5,12-Dihydroquino[2,3-*b*]acridine-7,14-dithione dimethylacetamide disolvate

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The title compound, $C_{20}H_{12}N_2S_2 \cdot 2C_4H_9NO$, is a solvated centrosymmetric pigment molecule (DTQ) connected to two dimethylacetamide (DMA) molecules through N—H···O hydrogen bonds. One DTQ molecule is surrounded by six DMA molecules in the crystal structure.

Comment

5,12-Dihydroquino[2,3-*b*]acridine-7,14-dithione, abbreviated to DTQ, is a thionated derivative of industrially important 5,12-dihydroquino[2,3-*b*]acridine-7,14-dione (QA) (Herbst & Hunger, 1997). QA is widely used as the red pigment in painting and imaging areas, whereas DTQ is characterized by an intense near-IR absorption and has thus attracted attention as an electronic material for laser printers as well as optical disks based upon GaAsAl laser diodes (Mizuguchi *et al.*, 1994). In order to study the generation mechanism of the near-IR absorption of DTQ, single crystals were previously grown from the vapor phase (Mizuguchi *et al.*, 1992). However, the crystals were found to be inactive in the near-IR region. In the present investigation, a further attempt was made to grow single crystals of a polymorphic form from solution in the expectation of isolating near-IR-active crystals. Contrary to our expectation, solvated crystals which possess no near-IR absorption were obtained from a dimethylacetamide (DMA) solution as described below.
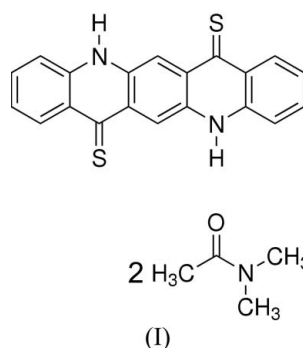

(I)

Fig. 1 shows an *ORTEPIII* (Burnett & Johnson, 1996) plot of the title compound, (I). The DTQ molecule is centrosymmetric and entirely planar, as characterized by the root-mean-square deviation of 0.03 Å from the least-squares plane (atoms C1–C10/N1). Two DMA molecules are connected to the DTQ molecule through N—H···O hydrogen bonds (Table 1). The DTQ molecules are stacked together with DMA molecules along the *a* axis with an interplanar distance of about 6.95 Å (Fig. 2). The DMA molecules are seen to block the direct formation of N—H···S hydrogen bonds between DTQ molecules and serve as the spacer. In other

words, one DTQ is surrounded by six DMA molecules in the crystal structure. Therefore, the absorption spectrum of (I) in the solid state is found to be quite similar to that in a DMA solution. A similar molecular packing is found in 2,9-dichlorinated DTQ with two DMA molecules (Senju *et al.*, 2005*b*) and also in 2,9-dichlorinated DTQ with two molecules of dimethylformamide (Senju *et al.*, 2005*a*).

Experimental

DTQ was synthesized by thionation of commercially available unsubstituted quinacridone using Lawesson's reagent (Rochat *et al.*, 1988). Single crystals of (I) were grown by gradual cooling of a DMA solution prepared at about 420 K. After 24 h, a number of dark-green prismatic single crystals were obtained.

Crystal data

$C_{20}H_{12}N_2S_2 \cdot 2C_4H_9NO$	$V = 636.4$ (3) Å^3
$M_r = 518.70$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.353$ Mg m^{-3}
$a = 7.353$ (2) Å	Cu $K\alpha$ radiation
$b = 8.328$ (2) Å	$\mu = 2.17$ mm^{-1}
$c = 11.832$ (3) Å	$T = 93.1$ K
$\alpha = 97.706$ (17)°	Prism, dark green
$\beta = 105.859$ (17)°	$0.20 \times 0.15 \times 0.10$ mm
$\gamma = 109.493$ (17)°	

Data collection

Rigaku R-AXIS RAPID-F Imaging Plate diffractometer	5445 measured reflections
	2166 independent reflections
ω scans	1941 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.051$
$T_{min} = 0.632$, $T_{max} = 0.805$	$\theta_{max} = 68.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1062P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.072$	$+ 1.0872P]$
$wR(F^2) = 0.202$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} < 0.001$
2166 reflections	$\Delta\rho_{max} = 2.03$ e Å^{-3}
171 parameters	$\Delta\rho_{min} = -0.63$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

| $D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$N1-\text{H}1N\cdots O1$	0.77 (4)	1.99 (4)	2.762 (4)	177 (4)

The N-bound H atom was found in a difference Fourier map and refined freely with an isotropic displacement parameter. The methyl H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and $U_{iso}(\text{H}) = 1.2U_{eq}(\text{C})$, but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.95 Å and $U_{iso}(\text{H}) = 1.2U_{eq}(\text{C})$. The highest residual density peak is located 1.00 Å from atom C11.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97*
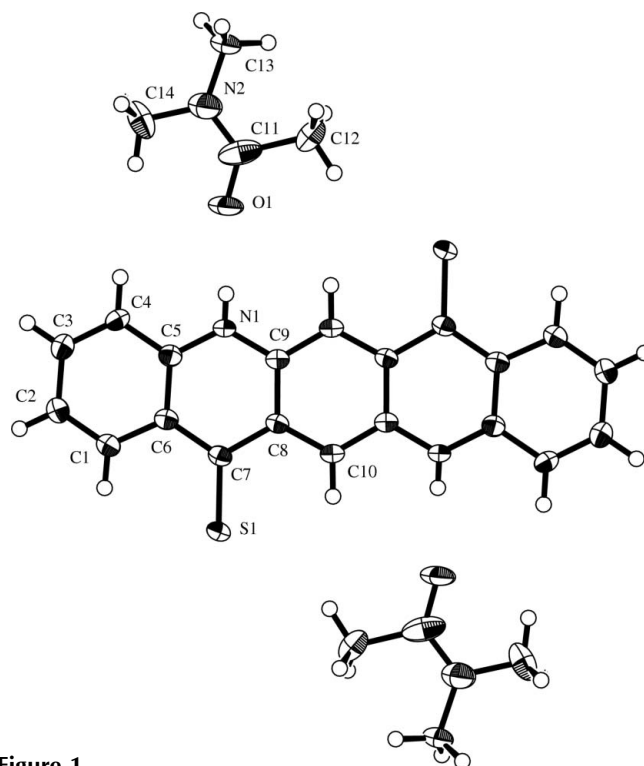
Figure 1
A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. The unlabeled atoms are related to labeled atoms by the symmetry code $(2 - x, 2 - y, 2 - z)$.
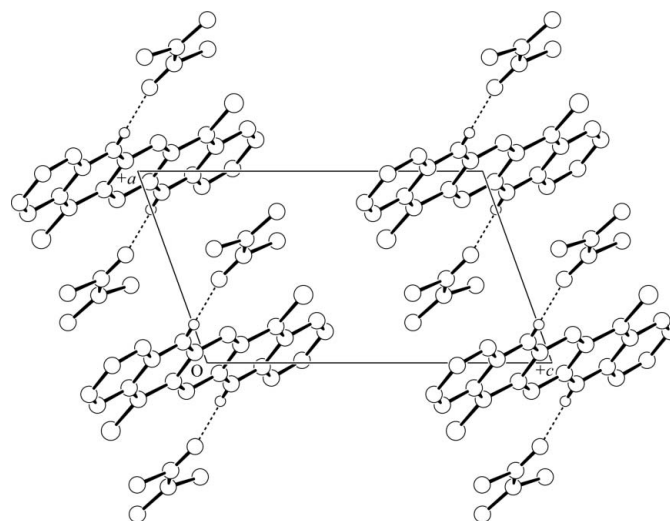
Figure 2
Projection down the *b* axis, showing the stacking of the DTQ molecules along the *a* axis. The dotted lines indicate hydrogen bonds. All the H atoms except for that of the NH group of DTQ have been omitted for clarity.

(Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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