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The monoclinic form of 2,9-dichloro-5,12-dihydroquino[2,3-*b*]acridine-7,14-dithione dimethylacetamide disolvate

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The title compound, $C_{20}H_{10}Cl_2N_2S_2\cdot 2C_4H_9NO$, is a dimethylacetamide (DMA) disolvate of DTQ-Cl, which is a thionated derivative of a 2,9-dichloroquinacridone pigment. The compound shows polymorphism and this paper reports the monoclinic form (space group $P2_1/c$, $Z = 4$). Two DMA molecules are hydrogen bonded *via* their O atoms to the NH group of DTQ-Cl. The molecular planes of the two DMA molecules are asymmetrically twisted with respect to the DTQ-Cl skeleton by 11.65 (8) and 31.58 (9)°.

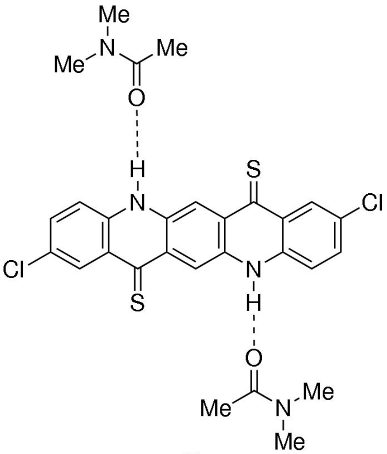
Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.137
Data-to-parameter ratio = 13.2

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

Comment

The title compound (DTQ-Cl·2DMA), (I), is a dimethylacetamide (DMA) disolvate of DTQ-Cl, which is a thionated derivative of 2,9-dichloroquinacridone known as an industrially important red pigment (Herbst & Hunger, 1997). The background of the present study has been set out in our earlier paper (Senju *et al.*, 2005*a*). We obtained three kinds of solvated crystals of DTQ-Cl. One was isolated from a dimethylformamide solution (Senju *et al.*, 2005*a*), and the other two polymorphic crystals were obtained from one single solution in DMA. The present report describes the structure of the monoclinic form, (I*a*), while that of the triclinic form, (I*b*), will be presented in the following paper (Senju *et al.*, 2005*b*).



(I)

Fig. 1 shows an *ORTEPIII* (Burnett & Johnson, 1996) plot of (I*a*) which includes two solvent molecules. The DTQ-Cl molecule is noncentrosymmetric and planar, as characterized by the mean standard deviation of 0.038 Å from the least-squares plane (C1–C20/N1/N2). The molecular planes of the two DMA molecules are asymmetrically twisted with respect to the skeleton of DTQ-Cl by 11.65 (8) and 31.58 (9)°.

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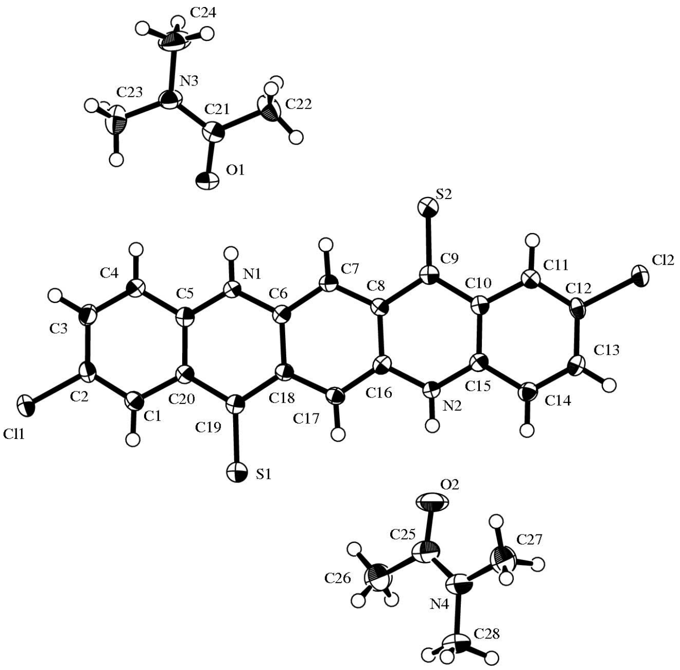

Figure 1
A view of the molecular structure of (I*a*), showing 50% probability displacement ellipsoids.

There are N—H···O intermolecular hydrogen bonds (Table 2) between the NH group of DTQ-Cl and the O atom of DMA. The geometrical features of the two N—H···O hydrogen bonds are slightly different, as also inferred by the asymmetric torsion angles between DMA and the DTQ-Cl skeleton. DTQ-Cl molecules are stacked along the *b* axis in such a way that the molecules of one column cross the others in the neighbouring column in a 'hunter's fence' fashion when viewed from the side (Fig. 2). DMA molecules also form their own columns and these are sandwiched by two columns of DTQ-Cl.

Experimental

DTQ-Cl was synthesized by thionation of commercially available 2,9-dichloroquinacridone, using Lawesson's reagent (Rochat *et al.*, 1988). Crystals of (I) were grown by gradual cooling from a dimethylacetamide solution prepared at about 420 K. Single crystals of both monoclinic and triclinic forms [(I*a*) and (I*b*), respectively] were obtained at the same time from one single solution. Both crystal forms appeared dark green. However, the crystal shapes were different, being needle for (I*a*) and platelet for (I*b*).

Crystal data

$C_{20}H_{10}Cl_2N_2S_2 \cdot 2C_4H_9NO$
$M_r = 587.58$
Monoclinic, $P2_1/c$
$a = 14.0463$ (12) Å
$b = 7.7507$ (7) Å
$c = 25.092$ (2) Å
$\beta = 90.446$ (6)°
$V = 2731.7$ (4) Å^3
$Z = 4$
$D_x = 1.429$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 19515 reflections
$\theta = 3.1$–68.3°
$\mu = 3.85$ mm^{-1}
$T = 93.1$ K
Needle, dark green
0.50 × 0.10 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID-F imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.321$, $T_{\max} = 0.681$
23140 measured reflections
4612 independent reflections
3911 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 68.2°$
$h = -16 \rightarrow 16$
$k = -7 \rightarrow 8$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.137$
$S = 1.09$
4612 reflections
350 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 2.5397P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.748 (3)	C6—C18	1.425 (3)
Cl2—C12	1.744 (3)	C7—C8	1.391 (3)
S1—C19	1.674 (3)	C8—C16	1.423 (3)
S2—C9	1.666 (2)	C8—C9	1.463 (3)
N1—C5	1.354 (3)	C9—C10	1.461 (3)
N1—C6	1.371 (3)	C10—C15	1.409 (3)
N2—C15	1.353 (3)	C10—C11	1.413 (4)
N2—C16	1.371 (3)	C11—C12	1.366 (3)
C1—C2	1.365 (4)	C12—C13	1.407 (4)
C1—C20	1.418 (4)	C13—C14	1.360 (4)
C2—C3	1.403 (4)	C14—C15	1.415 (3)
C3—C4	1.363 (4)	C16—C17	1.390 (4)
C4—C5	1.416 (4)	C17—C18	1.392 (3)
C5—C20	1.412 (3)	C18—C19	1.455 (3)
C6—C7	1.394 (3)	C19—C20	1.452 (3)
C5—N1—C6	122.5 (2)	C11—C10—C9	121.5 (2)
C15—N2—C16	122.7 (2)	C12—C11—C10	120.2 (2)
C2—C1—C20	120.3 (2)	C11—C12—C13	121.3 (2)
C1—C2—C3	121.4 (2)	C11—C12—Cl2	120.3 (2)
C1—C2—Cl1	119.6 (2)	C13—C12—Cl2	118.47 (19)
C3—C2—Cl1	118.96 (19)	C14—C13—C12	119.8 (2)
C4—C3—C2	119.8 (2)	C13—C14—C15	120.2 (2)
C3—C4—C5	120.2 (2)	N2—C15—C10	121.2 (2)
N1—C5—C20	120.8 (2)	N2—C15—C14	118.7 (2)
N1—C5—C4	119.0 (2)	C10—C15—C14	120.1 (2)
C20—C5—C4	120.2 (2)	N2—C16—C17	119.3 (2)
N1—C6—C7	119.4 (2)	N2—C16—C8	119.6 (2)
N1—C6—C18	119.7 (2)	C17—C16—C8	121.1 (2)
C7—C6—C18	120.8 (2)	C16—C17—C18	121.2 (2)
C8—C7—C6	121.2 (2)	C17—C18—C6	117.8 (2)
C7—C8—C16	117.8 (2)	C17—C18—C19	121.7 (2)
C7—C8—C9	121.7 (2)	C6—C18—C19	120.4 (2)
C16—C8—C9	120.5 (2)	C20—C19—C18	116.0 (2)
C10—C9—C8	115.9 (2)	C20—C19—S1	122.18 (19)
C10—C9—S2	122.15 (19)	C18—C19—S1	121.83 (19)
C8—C9—S2	121.94 (18)	C5—C20—C1	118.1 (2)
C15—C10—C11	118.4 (2)	C5—C20—C19	120.5 (2)
C15—C10—C9	120.1 (2)	C1—C20—C19	121.3 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1	0.88	1.89	2.747 (3)	164
N2—H2N···O2	0.88	1.89	2.772 (3)	176

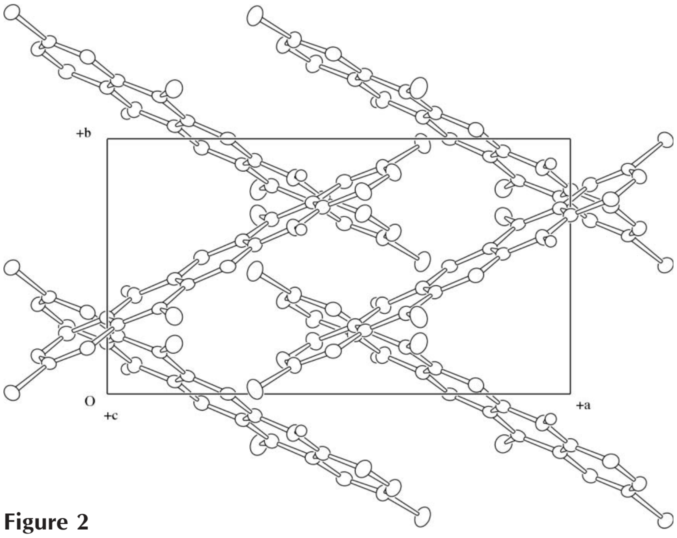

Figure 2
A projection down the *c* axis, showing the stacking of the DTQ-Cl molecules in (I*a*). The solvent DMA molecules have been omitted for clarity.

Methyl H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(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 N—H = 0.88 Å and C—H = 0.95 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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