Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2,9-Dichloroquino[2,3-*b*]acridine-7,14(5*H*,12*H*)-dithione dimethylformamide disolvate

Takatoshi Senju, Tomonori Hoki and Jin Mizuguchi*

Department of Applied Physics, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

Correspondence e-mail: mizu-j@ynu.ac.jp

Received 25 April 2005
Accepted 27 April 2005
Online 14 May 2005

Key indicators

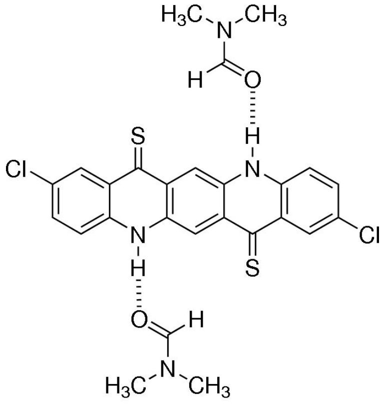
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.096
Data-to-parameter ratio = 12.5

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

The title compound, $C_{20}H_{10}Cl_2N_2S_2\cdot2C_3H_7NO$, is a dimethylformamide (DMF) disolvate of DTQ-Cl, which is a thionated pigment derivative of 2,9-dichloroquinacridone. The DTQ-Cl molecule is centrosymmetric and entirely planar. Two DMF molecules are hydrogen-bonded to DTQ-Cl, through the NH group of DTQ-Cl and the O atom of DMF. The molecular plane of DMF is twisted with respect to the skeleton of DTQ-Cl by 21.4 (1)°.

Comment

The title compound, (I), is a DMF disolvate of DTQ-Cl, which is a thionated derivative of 2,9-dichloroquinacridone known as an industrially important red pigment (Herbst & Hunger, 1997). We have previously reported that thionation of unsubstituted quinacridone brings about an intense near-IR absorption that can be utilized for laser printers, as well as optical disks based on GaAsAl laser diodes (Mizuguchi *et al.*, 1992, 1994). DTQ-Cl has, therefore, been synthesized in the expectation that it exhibits even better performance and stability for electronic applications. Since optical absorption in the solid state depends largely on intermolecular interactions, X-ray crystal structure analysis of DTQ-Cl is crucial. We obtained three types of solvated crystals: one was isolated from a DMF solution (present study) and the other two were from a single solution in dimethylacetamide (Senju *et al.*, 2005; Hoki *et al.*, 2005). This report deals with the title dimethylformamide solvate, DTQ-Cl·2DMF, (I).



(I)

Fig. 1 shows an *ORTEPIII* (Burnett & Johnson, 1996) plot of (I) including the two solvent molecules. The DTQ-Cl molecule is centrosymmetric and entirely planar, as characterized by the mean deviation of 0.006 Å from the least-squares plane (C1–C10/N1).

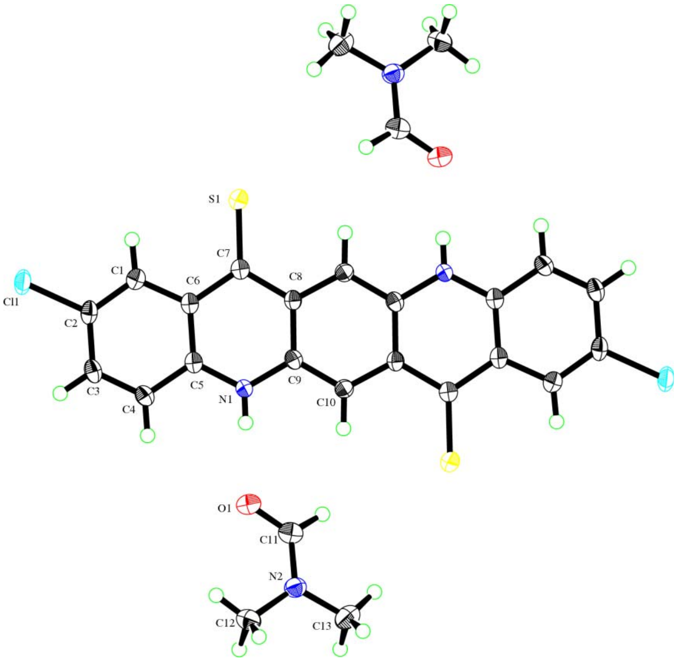


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry operator ($-x$, $2 - y$, $-z$).

There are N—H···O intermolecular hydrogen bonds between the NH group of DTQ-Cl and the O atom of DMF. As shown in Table 2, the N, H and O atoms are perfectly aligned, with an N···O distance of 2.769 (2) Å, indicating that this hydrogen bond is quite strong. The molecular plane of DMF is twisted with respect to the skeleton of DTQ-Cl by 21.4 (1)°. DTQ-Cl molecules are stacked along the b axis in a herringbone fashion.

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 of a dimethylformamide solution prepared at about 420 K.

Crystal data

$C_{20}H_{10}Cl_2N_2S_2{\cdot}2C_3H_7NO$
$M_r = 559.53$
Monoclinic, $C2/c$
$a = 33.257$ (4) Å
$b = 4.2682$ (6) Å
$c = 21.589$ (3) Å
$\beta = 123.872$ (7)°
$V = 2544.4$ (6) Å^3
$Z = 4$

$D_x = 1.461$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 9508 reflections
$\theta = 3.2$–68.3°
$\mu = 4.10$ mm^{-1}
$T = 93.1$ K
Needle, dark green
0.50 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID-F imaging plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.280$, $T_{max} = 0.815$
11 564 measured reflections

2123 independent reflections
1947 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.028$
$\theta_{max} = 68.2$°
$h = -40 \rightarrow 40$
$k = -4 \rightarrow 4$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.096$
$S = 1.10$
2123 reflections
170 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 3.2176P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.746 (2)	C4—C5	1.418 (3)
S1—C7	1.663 (3)	C5—C6	1.411 (3)
N1—C5	1.357 (2)	C9—C10	1.393 (2)
N1—C9	1.372 (2)	C8—C9	1.418 (3)
C1—C2	1.371 (3)	C8—C7	1.462 (2)
C1—C6	1.413 (2)	C8—C10^{i}	1.394 (3)
C2—C3	1.404 (4)	C7—C8	1.462 (2)
C3—C4	1.364 (3)	C7—C6	1.458 (3)
Cl1—C2—C1	119.9 (2)	C1—C6—C7	121.4 (2)
Cl1—C2—C3	118.4 (1)	C1—C6—C5	118.2 (2)
S1—C7—C8	121.7 (2)	C2—C3—C4	119.4 (2)
S1—C7—C6	122.9 (1)	C3—C4—C5	120.2 (2)
N1—C5—C6	121.2 (2)	C4—C5—C6	120.3 (2)
N1—C5—C4	118.5 (2)	C5—C6—C7	120.4 (2)
C9—N1—C5	122.2 (2)	C9—C8—C7	121.0 (2)
N1—C9—C8	119.8 (2)	C10—C9—C8	120.8 (2)
N1—C9—C10	119.4 (2)	C9—C10—C8^{i}	121.6 (2)
C1—C2—C3	121.7 (2)	C8—C7—C6	115.4 (2)
C6—C1—C2	120.1 (2)	C10^{i}—C8—C7	121.4 (2)

Symmetry code: (i) $-x$, $2 - y$, $-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1	0.82 (2)	1.95 (3)	2.769 (2)	180 (3)

The position of the imide H atom was found in a difference Fourier map and refined freely along with an isotropic displacement parameter. Methyl H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and U_{iso}(H) = 1.2U_{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 C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku, 2004); 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*.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Herbst, W. & Hunger, K. (1997). *Industrial Organic Pigments*, 2nd ed., pp. 454–474. Weinheim: VCH.

o1618 Senju *et al.* • $C_{20}H_{10}Cl_2N_2S_2{\cdot}2C_3H_7NO$ *Acta Cryst.* (2005). E**61**, o1617–o1619

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hoki, T., Senju, T. & Mizuguchi, J. (2005). *Acta Cryst.* E**61**. Submitted.
Mizuguchi, J. & Rihs, G. (1992). *Acta Cryst.* C**48**, 1553–1555.
Mizuguchi, J., Rochat, A. C. & Rihs, G. (1994). *Ber. Bunsenges. Phys. Chem.* **98**, 19–28.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC and Rigaku (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, Akishima, Tokyo, Japan.
Rochat, A. C., Jaffe, E. E. & Mizuguchi, J. (1988). US Patent No. 4 760 004.
Senju, T., Hoki, T. & Mizuguchi, J. (2005). *Acta Cryst.* E**61**. Submitted.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Acta Cryst. (2005). E**61**, o1617–o1619 Senju *et al.* • $C_{20}H_{10}Cl_2N_2S_2{\cdot}2C_3H_7NO$ **o1619**