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5′-Aminohydroxymethylene-1′,2′-dichloro-spiro[7*H*-pyrano[3,2-*c*;5,6-*c*′]dichromene-7,4′-cyclohex-2′-ene]-3′,6,6′,8-tetraone dimethylformamide disolvate, a spiro compound from the reaction of 4-hydroxycoumarin with 2,3-dichloro-5,6-dicyanobenzoquinone

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4-Hydroxycoumarin reacts with 2,3-dichloro-5,6-dicyanobenzoquinone to form the title compound, $C_{25}H_{11}Cl_2NO_8\cdot 2C_3H_7NO$, which crystallizes as an *N*,*N*-dimethylformamide disolvate. Two coumarin units are fused at their 3-position (through the spiro C atom) and at their 4-position (through an ether linkage) to give a planar moiety.

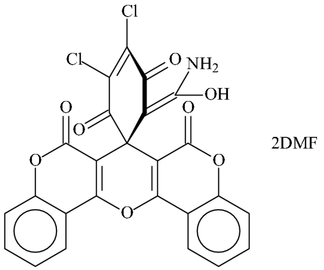
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.047
wR factor = 0.137
Data-to-parameter ratio = 14.0

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

Comment

When 4-hydroxycoumarin is reacted with *p*-benzoquinone, the H atom at the 4-position is replaced by the 3-benzoquinonyl group to yield compounds that can be reduced and then cyclodehydrated to form coumestans (Wagh & Usgaonkar, 1976). The reagent reacts similarly with *o*-benzoquinone (Srihari & Sundaramurthy, 1980). With 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), 4-hydroxycoumarin is instead converted to the dehydro dimer, 4,4′-dihydroxy-3,3′-dicoumarin (Buggle *et al.*, 1973). In our work, this reaction gave instead the title spiro compound (Fig. 1); we did not expect DDQ to react with functional groups (Walker & Hiebert, 1967; Fu & Harvey, 1978).



(I)

The two coumarin units are fused at their 4-positions through an ether oxygen linkage and also through their 3-positions through a C atom (which is part of a cyclohexene unit). The fused double-coumarin unit is planar and is essentially perpendicular to the cyclohexene unit. The compound features an unusual $=C(OH)(NH_2)$ substituent; a search of the Cambridge Structural Database (Version 5.25; Allen, 2002) revealed only six examples, five of these being drugs: tetracycline hydrochloride (Clegg & Teat, 2000), 6-methyleneoxytetracycline hydrobromide (Maria *et al.*, 1994), β-6-deoxy-oxytetracycline hydrochloride (Bordner, 1979), 4-deamino-4-hydroxy-4,11a-anhydrotetracycline methanol solvate (Barton *et al.*, 1977) and 5a-epi-6-thiatetracycline dimethylformamide (DMF) solvate (Prewo *et al.*, 1980). The exception is nitromalonamide, $(NH_2)(OH)C{=}C(NO_2)C(O)NH_2$ (Simonsen & Thorup, 1979). In the title compound, fused

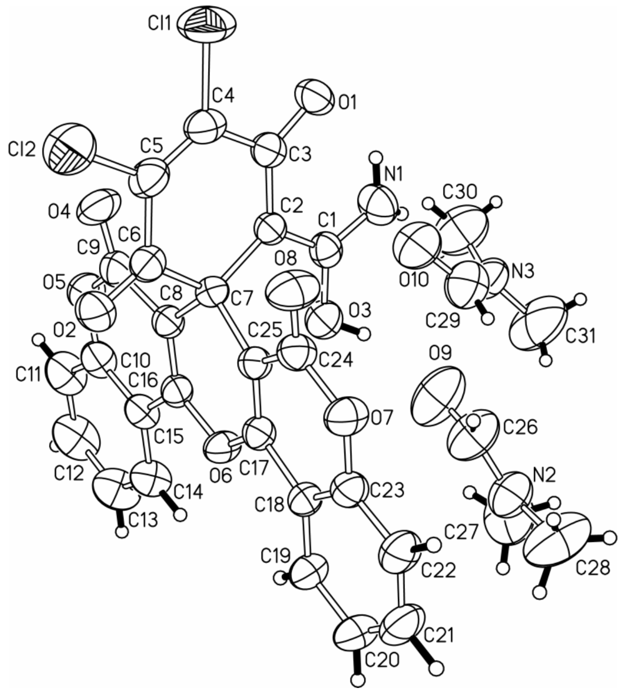


Figure 1
*ORTEP*II (Johnson, 1976) plot of $C_{25}H_{11}NO_8 \cdot 2DMF$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. The minor disordered DMF component is not shown.

coumarin molecules form centrosymmetric dimers through N—H···O hydrogen bonds, and the =C(OH)(NH_2) unit is further stabilized by O—H···O and N—H···O hydrogen bonding to the DMF molecules (Table 2).

Experimental

4-Hydroxycoumarin (0.4 g, 2.5 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (0.56 g, 2.4 mmol) were dissolved in ethanol (30 ml), and a drop of glacial acetic acid was added to the solution. The solution was heated under reflux for 24 h. The solvent was removed to afford a crude product that was purified by column chromatography on silica gel (1:5 methanol/chloroform). A pale yellow compound was isolated in about 60% yield. Crystals were grown from a DMF solution of the compound.

Crystal data

$C_{25}H_{11}Cl_2NO_8 \cdot 2C_3H_7NO$
$M_r = 670.44$
Triclinic, $P\bar{1}$
$a = 11.549$ (1) Å
$b = 11.720$ (1) Å
$c = 12.458$ (1) Å
$\alpha = 112.263$ (2)°
$\beta = 95.223$ (2)°
$\gamma = 91.974$ (2)°
$V = 1549.6$ (3) Å^3

$Z = 2$
$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 905 reflections
$\theta = 2.4$–25.7°
$\mu = 0.27$ mm^{-1}
$T = 295$ (2) K
Block, orange
0.31 × 0.22 × 0.16 mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: none
13 301 measured reflections
6683 independent reflections

3733 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 27.1°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.137$
$S = 1.00$
6683 reflections
479 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 0.1399P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C4	1.705 (2)	C1—C2	1.414 (3)
Cl2—C5	1.716 (2)	C2—C3	1.407 (3)
O1—C3	1.248 (2)	C2—C7	1.526 (3)
O2—C6	1.206 (3)	C3—C4	1.500 (3)
O3—C1	1.321 (3)	C4—C5	1.326 (3)
O4—C9	1.199 (3)	C5—C6	1.471 (3)
O5—C9	1.372 (3)	C6—C7	1.545 (3)
O5—C10	1.373 (3)	C7—C25	1.523 (3)
O6—C16	1.370 (2)	C7—C8	1.524 (3)
O6—C17	1.368 (2)	C8—C9	1.450 (3)
O7—C23	1.375 (3)	C17—C18	1.435 (3)
O7—C24	1.372 (3)	C17—C25	1.343 (3)
O8—C24	1.201 (3)	C24—C25	1.443 (3)
N1—C1	1.310 (3)		
C9—O5—C10	121.9 (2)	C7—C8—C9	116.4 (2)
C16—O6—C17	117.4 (2)	C7—C8—C16	124.0 (2)
C23—O7—C24	121.6 (2)	C9—C8—C16	119.6 (2)
O3—C1—N1	117.9 (2)	O4—C9—O5	117.7 (2)
O3—C1—C2	117.7 (2)	O4—C9—C8	124.8 (2)
N1—C1—C2	124.4 (2)	O5—C9—C8	117.5 (2)
C1—C2—C3	119.3 (2)	O5—C10—C11	116.8 (2)
C1—C2—C7	117.8 (2)	O5—C10—C15	121.9 (2)
C3—C2—C7	123.0 (2)	C10—C15—C16	116.2 (2)
O1—C3—C2	125.5 (2)	C14—C15—C16	124.6 (2)
O1—C3—C4	116.8 (2)	O6—C16—C8	123.6 (2)
C2—C3—C4	117.7 (2)	O6—C16—C15	113.8 (2)
C3—C4—C5	123.8 (2)	C8—C16—C15	122.6 (2)
Cl1—C4—C3	115.0 (2)	O6—C17—C18	114.0 (2)
Cl1—C4—C5	121.2 (2)	O6—C17—C25	123.6 (2)
C4—C5—C6	122.0 (2)	C18—C17—C25	122.4 (2)
Cl2—C5—C4	123.0 (2)	C17—C18—C19	124.3 (2)
Cl2—C5—C6	115.0 (2)	C17—C18—C23	116.7 (2)
O2—C6—C5	121.9 (2)	O7—C23—C18	121.6 (2)
O2—C6—C7	119.1 (2)	O7—C23—C22	116.9 (2)
C5—C6—C7	119.1 (2)	O7—C24—O8	117.0 (2)
C2—C7—C8	111.0 (2)	O7—C24—C25	118.2 (2)
C2—C7—C25	111.2 (2)	O8—C24—C25	124.8 (2)
C8—C7—C25	106.9 (2)	C7—C25—C17	123.6 (2)
C6—C7—C25	106.5 (2)	C7—C25—C24	117.1 (2)
C2—C7—C6	114.5 (2)	C24—C25—C17	119.3 (2)
C6—C7—C8	106.4 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O9	0.84 (1)	1.77 (2)	2.553 (3)	154 (3)
N1—H1n1···O10	0.84 (1)	2.05 (1)	2.845 (5)	158 (3)
N1—H1n1···O10′	0.84 (1)	2.17 (2)	2.96 (2)	159 (3)
N1—H1n2···O1$^{\rm i}$	0.85 (1)	2.39 (2)	3.008 (3)	130 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

One of the two DMF molecules is disordered over two sites; the two components are approximately related by a false rotation. For the major and minor components, the two C—O distances were restrained to be within 0.01 Å of each other; the six N—C distances were similarly restrained. Additionally, the C···C distances were restrained to be within 0.02 Å of each other, and the displacement parameters were restrained to be approximately isotropic. The four-atom molecules were restrained to lie in a plane to within 0.05 Å. The disorder refined to a 72 (1):28 (1) ratio. The hydroxy and amine H atoms were located and refined with distance restraints [O—H = N—H = 0.85 (1) Å and H···H = 1.39 (1) Å]. The displacement parameters were refined. All other H atoms were placed at calculated positions in the riding-model approximation ($C—H_{aromatic}$ = 0.93 Å and $C—H_{methyl}$ = 0.96 Å), with their displacement parameters set to 1.2 times U_{eq} of the parent atoms for the aromatic H atoms and to 1.5 times U_{eq} for the methyl H atoms. The methyl groups were rotated to fit the electron density.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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