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N-[9-(2-Ethoxycarbonylphenyl)-6-(ethylamino)-2,7-dimethyl-3-xanthenylidene]-ethylammonium Iodide Monohydrate

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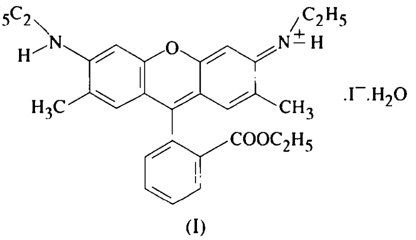
Abstract

The xanthene moiety in the title compound, $C_{28}H_{31}N_2O_3^+.I^-.H_2O$, is planar, with the attached phenyl ring twisted by −78.8 (6)° from the molecular plane. Of the two ethylamino groups, one is coplanar and the other makes a dihedral angle of 152.1 (5)° with the xanthene ring system. The positive charge of the cation is delocalized and both N—C_{sp^2} bonds show double-bond character.

Comment

Rhodamine 6G, with its excellent photophysical properties, has found extensive applications in tunable lasers (Hung & Meyer, 1992; Wittmann, Penzkofer & Baeumler, 1992), fluorescence depolarization diagnostic devices (Herz, 1974), photographic technology (Norland, Ames & Taylor, 1970) and electroluminescent devices (Johnson & McGrane, 1993). Furthermore, it can be used in concentrators of solar diagnostic devices (Batchelder, Zewail & Cole, 1979; Bhownik, Huri & Rohatgi-Mukherjee, 1987). The structure of the dye influences the molecular aggregation and also affects the absorption and emission properties (Ojeda, Katime, Ochoa & Arbeloa, 1988; Arbeloa, Aguirresacona & Arbeloa, 1989). In order to ascertain the structures of rhodamine 6G and its analogous complexes, we obtained crystals of the title compound, (I), from rhodamine 6G and $ZnI_2.6H_2O$ by ion-exchange reaction. To our knowledge, this is the first crystal structure report on a rhodamine derivative.



(I)

A displacement ellipsoid plot of (I) with the atom-numbering scheme is shown in Fig. 1. The xanthene moiety is planar, with the C2 atom showing the largest out-of-plane displacement of 0.075 (5) Å; the phenyl ring is twisted from the xanthene moiety by −78.8 (6)°. While one ethylamino group is almost coplanar with the xanthene moiety, the other makes a dihedral angle of 152.1 (5)° with it. The mean

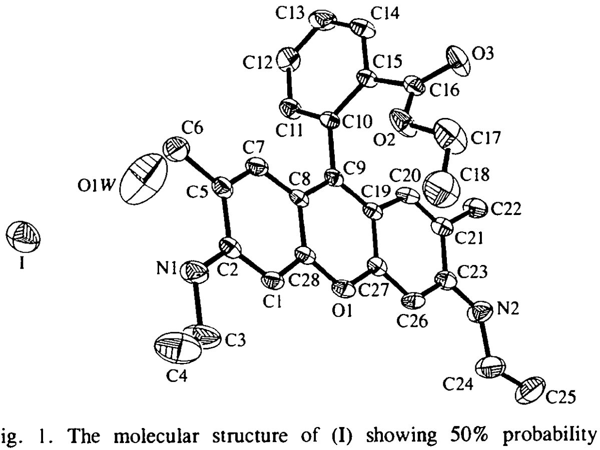


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are not shown.

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plane through the ethoxycarbonyl group makes an angle of 28.5 (2)° with the phenyl ring. The N1—C2 [1.348 (7) Å] and N2—C23 [1.347 (7) Å] bonds show partial double-bond character and the whole rhodamine 6G cation is delocalized. A very weak N—H···O hydrogen bond exists between N2 and the water molecule [N2···O1W^i 3.33 (1), H1N2···O1W^i 2.49 (6) Å and N2—H1N2···O1W^i 140 (5); symmetry code: (i) $x-\frac{1}{2}$, $-y+\frac{1}{2}$, $-z$]. Since the H atoms of the water molecule were not located, a complete description of the hydrogen bonding is not possible.

Experimental

To a 20 ml ethanol solution of rhodamine 6G (2.0 mmol), $ZnI_2.6H_2O$ (1.0 mmol) in 10 ml ethanol was added with stirring, followed by 20 ml acetonitrile. The reaction mixture was refluxed for 30 min. After cooling and filtration, the filtrate was left to evaporate at room temperature for several days whereupon crystals formed.

Crystal data

$C_{28}H_{31}N_2O_3^+.I^-.H_2O$
$M_r = 588.48$
Orthorhombic
Pbca
$a = 14.922\,(2)$ Å
$b = 15.157\,(2)$ Å
$c = 23.606\,(3)$ Å
$V = 5339.0\,(12)$ Å^3
$Z = 8$
$D_x = 1.464$ Mg m^{-3}
D_m not measured
Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections
$\theta = 2.06$–$12.55°$
$\mu = 1.235$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.70 × 0.58 × 0.48 mm
Pale red

Data collection

Siemens *P*4 diffractometer diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scans (*XSCANS*; Siemens, 1994)
$T_{\min} = 0.677$, $T_{\max} = 0.838$
6613 measured reflections
5499 independent reflections
3082 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.50°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 19$
$l = -1 \rightarrow 30$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.202$
$S = 0.984$
5497 reflections
368 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1225P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.75$ e Å^{-3}
$\Delta\rho_{\min} = -0.70$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—C28	1.370 (7)	C9—C10	1.501 (6)
C1—C2	1.386 (7)	C19—C20	1.411 (7)
C2—N1	1.348 (7)	C20—C21	1.343 (7)
C2—C5	1.433 (7)	C23—N2	1.347 (7)
C3—N1	1.477 (9)	C23—C26	1.393 (7)
C5—C7	1.345 (7)	C24—N2	1.452 (8)
C7—C8	1.425 (7)	C26—C27	1.382 (6)
C8—C9	1.376 (6)	C27—O1	1.365 (5)
C9—C19	1.416 (6)	C28—O1	1.371 (5)
C28—C1—C2	120.2 (5)	C20—C21—C23	117.9 (5)
C1—C2—C5	119.4 (5)	C26—C23—C21	120.3 (4)
C5—C7—C8	124.1 (5)	C27—C26—C23	119.4 (5)
C9—C8—C28	119.6 (4)	O1—C27—C19	121.1 (4)
C28—C8—C7	114.9 (4)	C26—C27—C19	122.1 (4)
C8—C9—C19	120.0 (4)	C1—C28—O1	116.8 (4)
C8—C9—C10	122.2 (4)	O1—C28—C8	120.5 (4)
C19—C9—C10	117.8 (4)	C27—O1—C28	120.2 (3)
C20—C19—C27	115.6 (4)	C2—N1—C3	124.2 (6)
C27—C19—C9	118.4 (4)	C23—N2—C24	124.8 (6)
C21—C20—C19	124.7 (5)		

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Thirteen H atoms were located from difference Fourier maps and their parameters were refined isotropically. Those of the other H atoms were fixed geometrically except for the two water H atoms which were not included in the calculations.

Programs for data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994); structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); structure refinement: *SHELXL*93 (Sheldrick, 1993); geometrical calculations: *PARST* (Nardelli, 1983).

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