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Crystal structure of (E)-2-(((6-bromopyridin-2-yl)methylene)amino)-3',6'-bis(ethylamino)-2',7'-dimethylspiro[isoindoline-1,9'-xanthen]-3-one—methanol (1:1), C₃₂H₃₀N₅O₂Br · CH₄O

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.20 × 0.10 × 0.05 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	2.17 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	71.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10106, 5746, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5452
$N(\text{param})_{\text{refined}}$:	389
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.78841(3)	0.30993(3)	0.45262(2)	0.03812(9)
O1	0.5079(2)	0.92439(15)	0.75648(9)	0.0403(4)
O2	0.48305(14)	0.23414(13)	0.78652(7)	0.0214(3)
O3	0.65957(15)	1.03774(16)	0.64014(9)	0.0317(3)
H3A	0.6267	0.9873	0.6732	0.047*
N1	0.67401(16)	0.46551(17)	0.55366(8)	0.0192(3)
N2	0.55231(16)	0.68183(16)	0.68502(8)	0.0165(3)
N3	0.49759(15)	0.67403(15)	0.75108(8)	0.0146(3)
N4	0.99018(18)	0.32581(18)	0.89547(8)	0.0205(3)
H4	1.066(3)	0.378(3)	0.8949(14)	0.030(7)*
N5	-0.01397(18)	0.08987(18)	0.66897(10)	0.0279(4)
H5	-0.0963	0.1137	0.6518	0.034*
C1	0.7342(2)	0.4802(2)	0.49153(10)	0.0236(4)
C2	0.7627(2)	0.6074(2)	0.45338(10)	0.0282(4)
H2	0.8061	0.6104	0.4098	0.034*
C3	0.7239(2)	0.7297(2)	0.48292(10)	0.0269(4)
H3	0.7403	0.8177	0.4591	0.032*
C4	0.6602(2)	0.7205(2)	0.54830(10)	0.0220(4)
H4A	0.6333	0.8015	0.5691	0.026*
C5	0.63772(18)	0.58638(19)	0.58200(9)	0.0171(3)
C6	0.57475(18)	0.56734(18)	0.65250(9)	0.0160(3)
H6	0.5522	0.4756	0.6725	0.019*
C7	0.4831(2)	0.80476(19)	0.78312(11)	0.0223(4)
C8	0.43612(19)	0.76900(19)	0.85567(10)	0.0190(3)
C9	0.4092(2)	0.8627(2)	0.91038(11)	0.0245(4)
H9	0.4148	0.9619	0.9030	0.029*
C10	0.3740(2)	0.8026(2)	0.97593(10)	0.0249(4)
H10	0.3563	0.8623	1.0136	0.030*

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Abstract

C₃₃H₃₄N₅O₃Br, triclinic, $P\bar{1}$ (no. 2), $a = 9.1179(2)$ Å, $b = 9.3291(3)$ Å, $c = 18.4706(6)$ Å, $\alpha = 91.187(3)^\circ$, $\beta = 95.764(2)^\circ$, $\gamma = 102.256(2)^\circ$, $Z = 2$, $V = 1526.15(8)$ Å³, $R_{\text{gt}}(F) = 0.0357$, $wR_{\text{ref}}(F^2) = 0.0954$, $T = 105.7(5)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C11	0.36478(19)	0.6531(2)	0.98620(10)	0.0215(4)
H11	0.3409	0.6147	1.0306	0.026*
C12	0.39081(18)	0.56050(19)	0.93086(9)	0.0169(3)
H12	0.3842	0.4609	0.9377	0.020*
C13	0.42680(17)	0.62134(18)	0.86546(9)	0.0141(3)
C14	0.46751(18)	0.54505(17)	0.79891(8)	0.0127(3)
C15	0.33898(18)	0.42390(17)	0.76589(8)	0.0132(3)
C16	0.19806(18)	0.45211(18)	0.73991(9)	0.0147(3)
H16	0.1847	0.5480	0.7433	0.018*
C17	0.07825(18)	0.34380(19)	0.70950(9)	0.0156(3)
C18	0.0989(2)	0.19716(19)	0.70335(9)	0.0189(3)
C19	0.2375(2)	0.16709(19)	0.73041(10)	0.0196(4)
H19	0.2519	0.0715	0.7279	0.024*
C20	0.35380(19)	0.27985(18)	0.76104(9)	0.0160(3)
C21	0.60718(18)	0.33800(18)	0.81394(9)	0.0149(3)
C22	0.73331(19)	0.28247(19)	0.83740(9)	0.0164(3)
H22	0.7289	0.1821	0.8335	0.020*
C23	0.86612(19)	0.37787(19)	0.86671(9)	0.0166(3)
C24	0.87216(19)	0.53128(19)	0.87018(9)	0.0172(3)
C25	0.74419(18)	0.58040(18)	0.84643(9)	0.0156(3)
H25	0.7482	0.6808	0.8491	0.019*
C26	0.60813(18)	0.48628(18)	0.81841(8)	0.0132(3)
C27	1.01381(19)	0.6371(2)	0.90126(11)	0.0235(4)
H27A	0.9978	0.7355	0.8996	0.035*
H27B	1.0948	0.6286	0.8732	0.035*
H27C	1.0393	0.6149	0.9508	0.035*
C28	−0.06798(19)	0.3804(2)	0.67836(10)	0.0212(4)
H28A	−0.0640	0.4828	0.6877	0.032*
H28B	−0.1501	0.3228	0.7008	0.032*
H28C	−0.0829	0.3587	0.6268	0.032*
C29	0.9925(2)	0.1710(2)	0.89142(11)	0.0259(4)
H29A	0.9780	0.1361	0.8408	0.031*
H29B	0.9103	0.1160	0.9158	0.031*
C30	1.1420(2)	0.1454(3)	0.92711(13)	0.0354(5)
H30A	1.2224	0.1928	0.9003	0.053*
H30B	1.1390	0.0419	0.9272	0.053*
H30C	1.1591	0.1853	0.9763	0.053*
C31	−0.0024(3)	−0.0619(2)	0.65998(14)	0.0384(5)
H31A	0.0972	−0.0645	0.6466	0.046*
H31B	−0.0757	−0.1089	0.6203	0.046*
C32	−0.0286(3)	−0.1485(3)	0.72768(19)	0.0579(8)
H32A	−0.0159	−0.2466	0.7189	0.087*
H32B	−0.1292	−0.1515	0.7396	0.087*
H32C	0.0428	−0.1021	0.7675	0.087*
C33	0.5438(2)	1.0981(2)	0.60476(12)	0.0307(4)
H33A	0.5853	1.1677	0.5707	0.046*
H33B	0.4988	1.1466	0.6402	0.046*
H33C	0.4683	1.0211	0.5793	0.046*

Source of material

All the solvents were of analytic grade. All starting materials were commercially available. The title compound was synthesized starting from rhodamine 6G hydrazide, which was obtained by following the synthetic procedure described in reference [5].

Rhodamine-6G hydrazide powder (2 mmol, 0.856 g) was dispersed in 20 mL absolute ethanol. 15 mL of an ethanol solution of 6-bromo-2-pyridinecarbaldehyde (2 mmol, 0.372 g) were added to the above dispersion. The reaction occurred immediately at the liquid-solid interface. After refluxing for 5 h under stirring, a light yellow precipitate appeared. The precipitate was filtered, washed 3 times with ethanol/water (1:1). Yield: *ca* 80%. The light yellow powder (0.05 mmol, 29.8 mg) was dissolved in methanol (15 mL) to give a light yellow solution which was left to evaporate slowly at room temperature. Light yellow crystals of the title compound were obtained after one week.

Experimental details

H atoms were added geometrically using riding models and refined isotropically. Their *U*_{iso} values were set to 1.2*U*_{eq} or 1.5*U*_{eq} of the parent atoms, as appropriate. The amine hydrogen atoms were initially freely refined. In a second step, after checking the geometry, one of them was treated as riding using the SHELXL AFIX 43 command.

Comment

Rhodamine derivatives have been widely studied as fluorescent probe and chemosensors [5–7] for their excellent spectroscopic properties [8, 9]. The title compound not only contains the xanthene fluorophore, but also has the ability to coordinate transition and rare-earth metals. So, it is in theory possible to obtain magnetic-fluorescent bifunctional complexes using this compound as a ligand. Multi-functional materials have attracted considerable attention in a variety of research fields [10, 11].

The asymmetric unit of the title compound consists of a rhodamine-based molecule and a methanol solvent molecule. The bond length of C6–N2 is 1.278(2) Å, which shows that the existence of Schiff base C=N. All bond lengths are within the expected range. Molecules of the rhodamine derivative are bridged *via* hydrogen bonding to methanol to form a one dimensional hydrogen-bonded chain, with methanol acting as a single hydrogen-bond donor and as a double acceptor. C–H···π and π–π contacts further stabilise the crystal structure.

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