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Crystal structure of (*E*)-2-(((6-bromopyridin-2-yl)methylene)amino)-3',6'-bis(diethylamino)spiro[isindoline-1,9'-xanthen]-3-one, C₃₄H₃₄N₅O₂Br

Table 1: Data collection and handling.

Crystal:	Needle, clear colorless
Size:	0.20 × 0.10 × 0.05 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	2.14 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	70°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	44776, 5403, 0.032
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5322
$N(\text{param})_{\text{refined}}$:	383
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], OLEX2 [4]

was facily synthesized from Rhodamine B by a two-step reaction.

The synthesis of the intermediate Rhodamine B hydrozone. Rhodamine B hydrozone is prepared according to the literature method [5]. To a 100 mL flask, Rhodamine B (2 mmol, 0.958 g) was dissolved in 30 mL ethanol. 3.0 mL (excess) hydrazine monohydrate (80%) was then added dropwise under vigorous stirring at room temperature. After the addition, the mixture was refluxed for 3 h. The solution changed from dark purple to light orange and became clear. Then the mixture was cooled and solvent was removed by reduced pressure. The resulting precipitate was filtered, washed 3 times with ethanol/water (1:1). Yield: ca. 70%.

The synthesis of the title compound. Rhodamine B hydrozone (1 mmol, 0.46 g) was dissolved in absolute ethanol, and ethanol solution of 6-bromo-2-pyridinecarbaldehyde (1 mmol, 0.186 g) was dropped to the solution under stirring. The mixture was refluxed for 5 h, and light purple precipitates appeared. The precipitate was filtered, washed 3 times with methanol/water (1:1). Yield: ca. 80%. The light purple product (0.05 mmol, 31.2 mg) was dissolved in ethanol/dichloromethane (1:1) (10 mL) to give a colorless solution to evaporate slowly at room temperature. After several days, colorless needle crystals appeared. Yield: ca. 70%.

Experimental details

The H atoms were added geometrically using riding models. Their U_{iso} values were set to 1.2 U_{eq} of the parent C and N

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Abstract

C₃₄H₃₄N₅O₂Br, orthorhombic $Pca2_1$ (no. 29), $a = 21.3626(13)$ Å, $b = 11.8358(8)$ Å, $c = 12.0998(9)$ Å, $Z = 4$, $V = 3059.38(4)$ Å³, $R_{\text{gt}}(F) = 0.0507$, $wR_{\text{ref}}(F^2) = 0.1401$, $T = 173$ 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.

Source of materials

All starting materials are commercially available, and are used without further purification. The title compound

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Br1	0.71823(3)	0.43127(7)	0.52183(7)	0.0704(3)
C1	0.6900(2)	0.5235(5)	0.4019(5)	0.0488(13)
C2	0.7302(3)	0.5440(6)	0.3156(8)	0.0650(19)
H2	0.7713	0.5132	0.3140	0.078*
C3	0.7083(4)	0.6107(7)	0.2324(9)	0.078(2)
H3	0.7348	0.6289	0.1719	0.093*
C4	0.6474(3)	0.6522(5)	0.2354(6)	0.0581(16)
H4	0.6318	0.6985	0.1775	0.070*
C5	0.6103(2)	0.6242(4)	0.3251(5)	0.0389(11)
C6	0.5445(2)	0.6589(4)	0.3331(4)	0.0362(10)
H6	0.5185	0.6315	0.3908	0.043*
C7	0.4425(2)	0.8307(4)	0.1764(4)	0.0370(10)
C8	0.3745(2)	0.8360(4)	0.1875(4)	0.0363(10)
C9	0.3310(3)	0.8944(4)	0.1232(5)	0.0448(12)
H9	0.3440	0.9398	0.0627	0.054*
C10	0.2687(3)	0.8844(5)	0.1501(6)	0.0553(15)
H10	0.2382	0.9234	0.1074	0.066*
C11	0.2495(3)	0.8186(5)	0.2381(6)	0.0553(15)
H11	0.2062	0.8127	0.2547	0.066*
C12	0.2932(2)	0.7602(4)	0.3034(5)	0.0461(13)
H12	0.2803	0.7165	0.3652	0.055*
C13	0.3557(2)	0.7686(3)	0.2750(4)	0.0343(9)
C14	0.4111(2)	0.7094(3)	0.3288(4)	0.0315(9)
C15	0.4065(2)	0.5829(3)	0.3154(4)	0.0309(9)
C16	0.4107(3)	0.5312(4)	0.2116(4)	0.0405(11)
H16	0.4187	0.5768	0.1486	0.049*
C17	0.4037(3)	0.4168(4)	0.1976(5)	0.0444(12)
H17	0.4067	0.3855	0.1255	0.053*
C18	0.3923(3)	0.3459(4)	0.2870(5)	0.0428(12)
C19	0.3873(2)	0.3962(4)	0.3923(5)	0.0410(11)
H19	0.3783	0.3509	0.4551	0.049*
C20	0.3956(2)	0.5117(4)	0.4041(4)	0.0341(9)
C21	0.40575(18)	0.6615(3)	0.5321(4)	0.0318(9)
C22	0.4079(2)	0.6897(4)	0.6436(4)	0.0360(10)
H22	0.3999	0.6333	0.6977	0.043*
C23	0.4218(2)	0.8003(4)	0.6773(4)	0.0368(10)
C24	0.4358(3)	0.8800(4)	0.5937(4)	0.0404(11)
H24	0.4471	0.9551	0.6133	0.048*
C25	0.4330(2)	0.8490(4)	0.4836(4)	0.0362(10)
H25	0.4417	0.9045	0.4290	0.043*
C26	0.4180(2)	0.7393(4)	0.4488(4)	0.0313(9)
C27	0.3775(4)	0.1550(5)	0.3666(7)	0.074(2)
H27A	0.4017	0.1833	0.4306	0.089*
H27B	0.3935	0.0789	0.3477	0.089*
C28	0.3103(5)	0.1461(10)	0.3980(10)	0.109(3)
H28A	0.2951	0.2201	0.4224	0.163*
H28B	0.3057	0.0913	0.4582	0.163*
H28C	0.2859	0.1210	0.3340	0.163*
C29	0.3928(4)	0.1801(5)	0.1620(6)	0.0635(17)
H29A	0.4027	0.0987	0.1692	0.076*
H29B	0.4281	0.2167	0.1227	0.076*
C30	0.3339(4)	0.1933(5)	0.0939(6)	0.0643(17)
H30A	0.2992	0.1542	0.1306	0.096*
H30B	0.3405	0.1605	0.0204	0.096*
H30C	0.3238	0.2737	0.0865	0.096*
C31	0.4401(3)	0.9426(5)	0.8228(5)	0.0573(16)
H31A	0.4749	0.9703	0.7761	0.069*
H31B	0.4553	0.9387	0.9000	0.069*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C32	0.3859(5)	1.0254(5)	0.8163(7)	0.080(3)
H32A	0.3761	1.0407	0.7386	0.120*
H32B	0.3976	1.0961	0.8531	0.120*
H32C	0.3492	0.9929	0.8529	0.120*
C33	0.4063(3)	0.7474(4)	0.8729(4)	0.0433(12)
H33A	0.3723	0.6980	0.8453	0.052*
H33B	0.3901	0.7886	0.9381	0.052*
C34	0.4597(3)	0.6755(5)	0.9082(6)	0.0545(13)
H34A	0.4764	0.6348	0.8440	0.082*
H34B	0.4454	0.6210	0.9637	0.082*
H34C	0.4926	0.7231	0.9400	0.082*
N1	0.6315(2)	0.5602(4)	0.4082(4)	0.0428(10)
N2	0.52310(18)	0.7272(3)	0.2597(4)	0.0366(8)
N3	0.46293(18)	0.7576(3)	0.2596(3)	0.0335(8)
N4	0.3870(3)	0.2300(4)	0.2733(5)	0.0601(14)
N5	0.4221(2)	0.8298(3)	0.7865(4)	0.0444(10)
O1	0.39164(17)	0.5499(2)	0.5118(3)	0.0406(7)
O2	0.47625(19)	0.8795(3)	0.1113(3)	0.0473(9)

atoms, and 1.5*U*_{eq} of the parent O atoms. The classical Flack parameter was 0.00(3) [2].

Discussion

In recent years, there has been a great interest in the development of fluorescent chemosensors and fluorescent probes. Rhodamine B derivatives have attracted great attention of scientists by virtue of their long-wavelength emission and availability [5–10].

In this paper, we report a rhodamine B pyridyl aroyl-hydrozone compound. The asymmetric unit contains a neutral molecule in a ring-closed form. The amide C=O bond distance is 1.214(6) Å, indicative of the keto form of the amide (*cf.* the figure). The dihedral angle between the least-square plane of the xanthenyl moiety and the pyridyl aroylhydrozone group is 84.69°. There are no obvious hydrogen bonding interactions or π – π interactions between adjacent molecules. Bond lengths and angles in the title molecule are in the expected ranges [11]. The title molecule may have some applications as the nitrogen atoms in pyridine ring and imine, oxygen atom in carbonyl group have strong coordination ability to transition metals and rare-earth metals [12].

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