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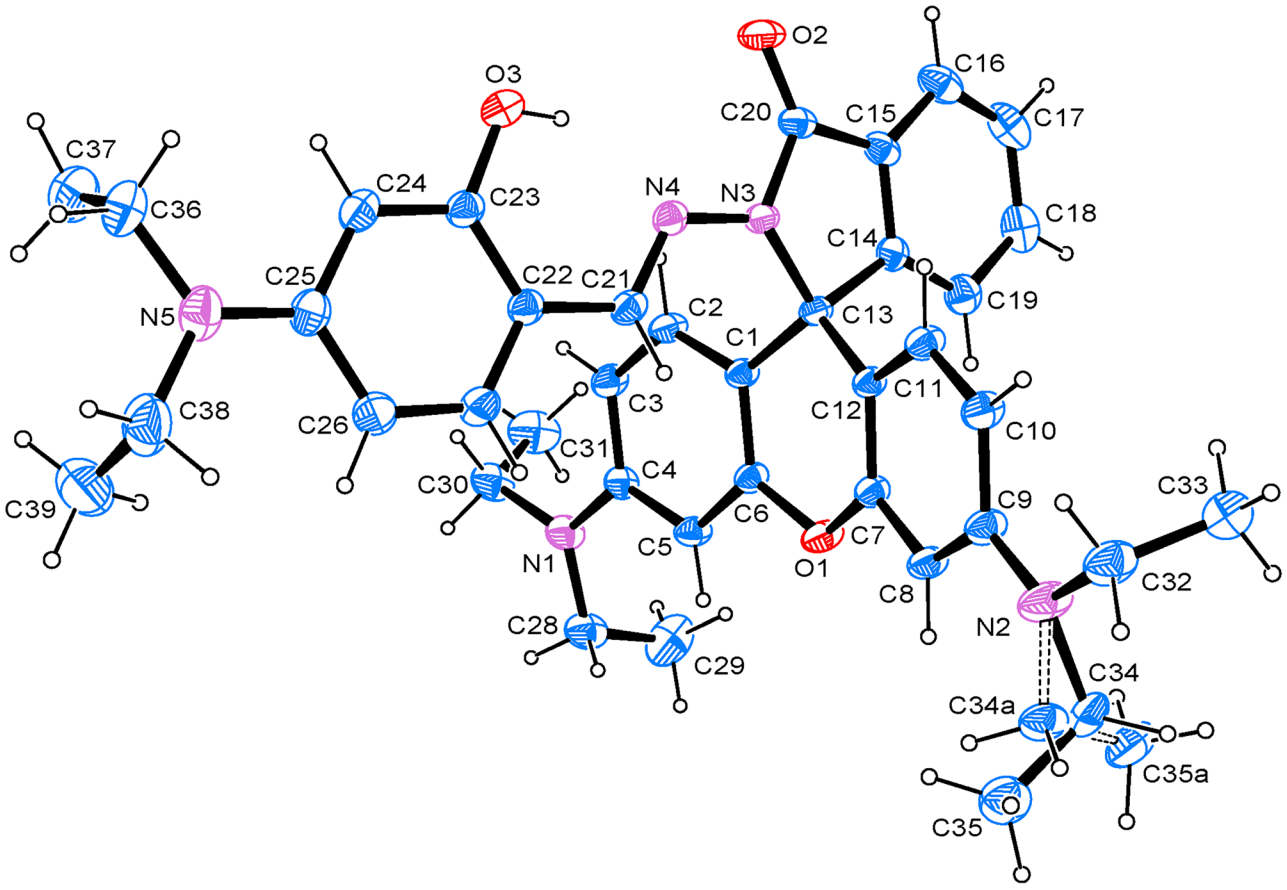
The crystal structure of (*E*)-3′,6′-bis(diethylamino)-2-((5-(diethylamino)-2-hydroxybenzylidene)amino)spiro[isoindoline-1,9′-xanthen]-3-one, $C_{39}H_{45}N_5O_3$



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Abstract

$C_{33}H_{31}BrN_4O_3$, monoclinic, $P2_1/n$ (no. 14), a = 11.8558(12) Å, b = 12.1159(11) Å, c = 24.014(2) Å, β = 94.812(2)°, V = 3437.3(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0574, w$R_{ref}(F^2)$ = 0.1725, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were purchased from commercial sources and used as received. A mixture of rhodamine B hydrazide (1 mmol), 5-(diethylamino)-2-hydroxybenzaldehyde

Table 1: Data collection and handling.

Crystal:	Pink acicular
Size:	0.19 × 0.18 × 0.15 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17210, 6114, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3313
$N(param)_{refined}$:	451
Programs:	Bruker [1], SHELX [2, 3], WINGX/ORTEP [4]

(1 mmol), and CH_3OH (50 mL) was added in a round-bottomed flask (100 mL), and refluxed for 5.0 h. The solution was cooled and filtered. Finally, the title crystal was precipitated by controlling solvent volatilization.

Experimental details

All H-atoms bonded to C atoms were placed geometrically and refined using a riding model with common isotropic displacement factors $U_{iso}(H) = 1.2$ or 1.5 U_{eq}(parent C-atom).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.18320 (13)	0.80843 (13)	0.14611 (8)	0.0724 (5)
O2	−0.17777 (16)	0.42182 (15)	0.18188 (9)	0.0859 (6)
O3	−0.03513 (18)	0.41609 (16)	0.32932 (8)	0.0854 (6)
H3A	−0.045581	0.434037	0.296369	0.128*
N1	0.48292 (18)	0.54753 (19)	0.14314 (10)	0.0772 (7)
N2	−0.0588 (2)	1.09432 (19)	0.20122 (13)	0.0989 (8)
N3	−0.04574 (16)	0.56191 (15)	0.18734 (9)	0.0551 (5)
N4	−0.01804 (17)	0.54172 (16)	0.24265 (9)	0.0578 (5)
N5	0.1782 (3)	0.5081 (2)	0.49866 (12)	0.0954 (8)
C1	0.13623 (19)	0.61509 (19)	0.15165 (10)	0.0529 (6)
C2	0.1784 (2)	0.5090 (2)	0.15437 (11)	0.0671 (7)
H2	0.128351	0.450805	0.158113	0.080*
C3	0.2911 (2)	0.4857 (2)	0.15179 (12)	0.0697 (8)
H3	0.315532	0.412805	0.154309	0.084*
C4	0.3697 (2)	0.5698 (2)	0.14543 (11)	0.0601 (7)
C5	0.3280 (2)	0.6781 (2)	0.14329 (11)	0.0626 (7)
H5	0.377275	0.736808	0.139272	0.075*
C6	0.2137 (2)	0.69823 (19)	0.14716 (10)	0.0548 (6)
C7	0.0772 (2)	0.83598 (19)	0.16174 (10)	0.0564 (6)
C8	0.0608 (2)	0.9466 (2)	0.17266 (12)	0.0672 (7)
H8	0.119304	0.996337	0.168731	0.081*
C9	−0.0418 (2)	0.9849 (2)	0.18943 (12)	0.0695 (8)
C10	−0.1274 (2)	0.9062 (2)	0.19416 (12)	0.0720 (8)
H10	−0.197328	0.928293	0.205110	0.086*
C11	−0.1091 (2)	0.7976 (2)	0.18288 (11)	0.0651 (7)
H11	−0.167449	0.747485	0.186611	0.078*
C12	−0.00706 (18)	0.75860 (18)	0.16604 (10)	0.0516 (6)
C13	0.01094 (18)	0.63932 (18)	0.15065 (10)	0.0524 (6)
C14	−0.0505 (2)	0.6084 (2)	0.09497 (11)	0.0560 (6)
C15	−0.1268 (2)	0.5255 (2)	0.10074 (12)	0.0628 (7)
C16	−0.1913 (2)	0.4818 (3)	0.05510 (16)	0.0856 (9)
H16	−0.242205	0.424758	0.059567	0.103*
C17	−0.1782 (3)	0.5245 (4)	0.00373 (16)	0.1004 (11)
H17	−0.220896	0.496637	−0.027387	0.120*
C18	−0.1023 (3)	0.6086 (3)	−0.00264 (14)	0.0939 (10)
H18	−0.094742	0.637162	−0.038088	0.113*
C19	−0.0365 (2)	0.6520 (2)	0.04324 (13)	0.0777 (8)
H19	0.015082	0.708535	0.038859	0.093*
C20	−0.1241 (2)	0.4935 (2)	0.15964 (13)	0.0629 (7)
C21	0.0549 (2)	0.6008 (2)	0.27140 (11)	0.0588 (7)
H21	0.088481	0.660351	0.254751	0.071*
C22	0.0852 (2)	0.5760 (2)	0.32906 (11)	0.0580 (7)
C23	0.0406 (2)	0.4859 (2)	0.35616 (12)	0.0639 (7)

Table 2: (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C24	0.0740 (2)	0.4632 (2)	0.41131 (13)	0.0737 (8)
H24	0.044464	0.401347	0.427846	0.088*
C25	0.1502 (3)	0.5295 (3)	0.44299 (13)	0.0741 (8)
C26	0.1950 (3)	0.6208 (2)	0.41589 (13)	0.0795 (8)
H26	0.247084	0.667029	0.435338	0.095*
C27	0.1615 (2)	0.6414 (2)	0.36050 (13)	0.0735 (8)
H27	0.191850	0.702322	0.343525	0.088*
C28	0.5610 (2)	0.6323 (3)	0.12866 (15)	0.0907 (10)
H28A	0.637494	0.607982	0.139834	0.109*
H28B	0.547052	0.698424	0.149816	0.109*
C29	0.5532 (3)	0.6609 (3)	0.06810 (18)	0.1354 (16)
H29A	0.571743	0.597194	0.046886	0.203*
H29B	0.605349	0.719389	0.061969	0.203*
H29C	0.477599	0.684395	0.056439	0.203*
C30	0.5256 (2)	0.4328 (3)	0.14739 (15)	0.0926 (9)
H30A	0.606090	0.434067	0.158569	0.111*
H30B	0.488389	0.394405	0.176227	0.111*
C31	0.5063 (3)	0.3722 (3)	0.09516 (18)	0.1279 (14)
H31A	0.427217	0.373848	0.082831	0.192*
H31B	0.530260	0.297001	0.100831	0.192*
H31C	0.548891	0.405630	0.067341	0.192*
C32	−0.1672 (3)	1.1348 (3)	0.22181 (15)	0.0983 (10)
H32A	−0.193901	1.080918	0.247509	0.118*
H32B	−0.152513	1.203018	0.242322	0.118*
C33	−0.2562 (3)	1.1544 (3)	0.17693 (16)	0.1096 (11)
H33A	−0.230124	1.206990	0.151008	0.164*
H33B	−0.322360	1.182702	0.192492	0.164*
H33C	−0.274562	1.086287	0.157833	0.164*
C34[a]	0.013 (2)	1.1821 (18)	0.1716 (9)	0.093 (7)
H34A[a]	0.050792	1.149991	0.141003	0.112*
H34B[a]	−0.032076	1.244552	0.157952	0.112*
C35[a]	0.0968 (14)	1.2138 (12)	0.2196 (5)	0.104 (4)
H35A[a]	0.056821	1.243443	0.249398	0.156*
H35B[a]	0.148001	1.268389	0.207446	0.156*
H35C[a]	0.138708	1.149740	0.232697	0.156*
C34A[b]	0.0297 (12)	1.1737 (10)	0.1992 (5)	0.082 (3)
H34C[b]	0.102012	1.140447	0.211437	0.099*
H34D[b]	0.016767	1.235261	0.223653	0.099*
C35A[b]	0.0304 (7)	1.2126 (7)	0.1405 (5)	0.108 (3)
H35D[b]	0.037308	1.150376	0.116214	0.161*
H35E[b]	0.093256	1.261556	0.137441	0.161*
H35F[b]	−0.038921	1.250952	0.129801	0.161*
C36	0.1480 (3)	0.4027 (3)	0.52286 (14)	0.1031 (11)
H36A	0.069941	0.385550	0.510537	0.124*
H36B	0.153436	0.409525	0.563241	0.124*
C37	0.2219 (3)	0.3094 (3)	0.50717 (17)	0.1225 (13)
H37A	0.224574	0.307957	0.467339	0.184*
H37B	0.191460	0.240885	0.519363	0.184*
H37C	0.296889	0.319429	0.524762	0.184*
C38	0.2560 (5)	0.5800 (3)	0.53217 (16)	0.1288 (15)
H38A	0.238179	0.576102	0.570819	0.155*
H38B	0.243665	0.655494	0.519679	0.155*
C39	0.3760 (5)	0.5527 (4)	0.5295 (2)	0.175 (2)
H39A	0.389725	0.478919	0.542970	0.263*
H39B	0.421622	0.603510	0.552294	0.263*
H39C	0.395025	0.557852	0.491528	0.263*

[a]Occupancy: 0.368 (14), [b]Occupancy: 0.614 (14).

Comment

Rhodamine derivatives have attracted much attention in the design of chemosensors or chemodosimeters for metal ions [5]. Particularly, rhodamine hydrazones bearing a 2-hydroxybenzaldehyde unit may act as fluorescent probes for Cu^{2+} or Hg^{2+} [6, 7]. So, the synthesis and crystal structure of the title compound are of great significance to studying the application.

The ORTEP diagram is presented in the figure. Bond lengths and angles are all in the expected ranges [8, 9]. It can be seen from the figure that C13, C14, C15, C20, and N3 atoms form a five-membered heterocyclic ring, indicating that the title compound exists in the form of a closed spiro ring. The C=N of the title molecule exhibits an *E* configuration. The bond length of C21=N4 is 1.280(3) Å, which is similar to those reported in the literature [8, 9].

Intramolecular and intermolecular hydrogen bonding exist in the crystal structure of the title compound. The oxygen atom O3 provides one intramolecular hydrogen bond to N4 (O2···N4 = 2.600(3) Å). The carbon atom C30 provides one intermolecular hydrogen bond to O2′ of another molecule (C30···O2′ = 3.548(4) Å; ′ = $x + 1$, y, z).

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *SAINT*, *APEX*2 and *SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2012.
2. Sheldrick G. M. *SHELXTL* – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Farrugia L. J. WINGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
5. Chen X., Pradhan T., Wang F., Kim J. S., Yoon J. Fluorescent chemosensors based on spiroring-opening of xanthenes and related derivatives. *Chem. Rev.* 2012, *112*, 1910–1956.
6. Yang Y., Gao C.-Y., Li T., Chen J. A tetraphenylethene-based rhodamine hydrazone chemosensor for colorimetric and reversible detection of Cu^{2+}. *ChemistrySelect* 2016, *1*, 4577–4581.
7. Dong M., Tang J., Lv Y., Liu Y., Wang J., Wang T., Bian J., Li C. A dual-function fluorescent probe for Hg (II) and Cu (II) ions with two mutually independent sensing pathways and its logic gate behavior. *Spectrochim. Acta* 2020, *226*, 117645.
8. Yuan J. Crystal structure of (*E*)-2-(3,6-bis(ethylamino)-2,7-dimethyl-9*H*-xanthen-9-yl)- *N*′-((6-methylpyridin-2-yl) methylene)benzohydrazide – methanol (1/1), $C_{34}H_{37}N_5O_3$. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 1091–1093.
9. Yang M., Meng W., Liu X., Su N., Zhou J., Yang B. A selective colorimetric and fluorescent chemosensor for Cu^{2+} in living cells. *RSC Adv.* 2014, *4*, 22288–22293.