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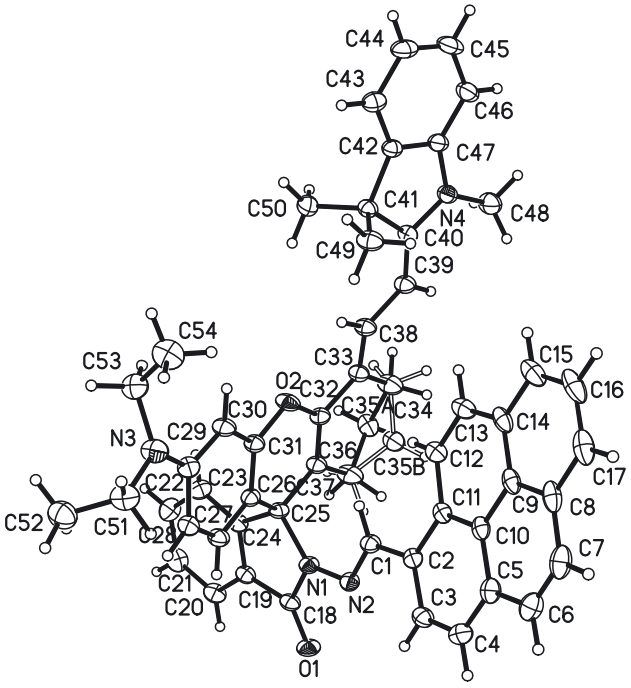
Crystal structure of (4′*E*)-6′-(diethylamino)-2-[(*E*)-[(pyren-1-yl)methylidene]amino]-4′-{2-[(2*E*)-1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene]ethylidene}-1′,2,2′,3,3′,4′-hexahydrospiro[isoindole-1,9′-xanthene]-3-one, $C_{54}H_{48}N_4O_2$



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Abstract

$C_{54}H_{48}N_4O_2$, triclinic, $P\bar{1}$ (no. 2), a = 11.1883(5) Å, b = 13.5364(5) Å, c = 14.3412(5) Å, α = 105.885(3)°, β = 97.710(3)°, γ = 94.126(3)°, Z = 2, V = 2056.64(14) Å^3, $R_{gt}(F)$ = 0.0685, $wR_{ref}(F^2)$ = 0.1606, T = 293(2) K.

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The asymmetric unit of the molecular structure is shown in the figure. Table 1 contains crystallographic data and

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	SuperNova
θ_{max}, completeness:	29.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18,679, 9577, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6192
$N(param)_{refined}$:	556
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were of reagent grade and used without further purification. The title compound was synthesized by a four-step reaction according to the references [5–7].

The synthesis of the first intermediate is a condensation reaction. The detailed steps are as follows: first, cyclohexanone (1.98 mL) was added dropwise to concentrated sulfuric acid (20.0 mL) and cooled down to 0 °C Then, 2-(4-diethylamino-hydroxybenzoyl) benzoic acid (3.00 g, 9.6 mmol) was added in portions under vigorous stirring. The reaction mixture was heated at 90 °C for 3 h, cooled down and poured onto crushed ice (150.0 g). Red precipitate appeared immediately as soon as perchloric acid (2.0 mL, 70%) was added, which was filtered and washed several times with cold water to obtain a red solid. Yield: ca. 94%.

The synthesis of the second intermediate 2-[(*E*)-2-[9-(2-carboxyphenyl)-6-(diethylamino)-2,3,4,9-tetrahydro-1*H*-xanthen-4-yl]ethenyl]-1,3,3-trimethyl-3*H*-indol-1-ium is a condensation reaction, too. The red solid (2.4 g, 6.38 mmol) obtained in the first step and fisher aldehyde (1.28 g,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.33412 (15)	0.98971 (13)	0.19667 (13)	0.0469 (4)
O2	0.78771 (16)	0.73548 (13)	0.24706 (11)	0.0446 (4)
N1	0.48253 (17)	0.88602 (14)	0.22453 (14)	0.0343 (4)
N2	0.40803 (16)	0.82515 (14)	0.25996 (13)	0.0334 (4)
N3	0.9082 (2)	0.90937 (18)	0.58565 (15)	0.0519 (6)
N4	0.89884 (18)	0.29127 (15)	0.02062 (14)	0.0397 (5)
C1	0.4486 (2)	0.74420 (18)	0.27677 (16)	0.0354 (5)
H1	0.522951	0.726360	0.259212	0.043*
C2	0.3809 (2)	0.67975 (17)	0.32272 (16)	0.0336 (5)
C3	0.2820 (2)	0.71470 (18)	0.36679 (17)	0.0397 (6)
H3	0.255214	0.776569	0.361141	0.048*
C4	0.2236 (2)	0.6601 (2)	0.41815 (18)	0.0446 (6)
H4	0.157191	0.685124	0.445767	0.054*
C5	0.2617 (2)	0.56782 (19)	0.42985 (17)	0.0407 (6)
C6	0.2063 (3)	0.5114 (2)	0.48726 (18)	0.0501 (7)
H6	0.141512	0.536260	0.517367	0.060*
C7	0.2459 (3)	0.4237 (2)	0.49844 (19)	0.0544 (7)
H7	0.208539	0.389547	0.536856	0.065*
C8	0.3437 (3)	0.38123 (19)	0.45301 (18)	0.0475 (7)
C9	0.4016 (2)	0.43476 (17)	0.39556 (16)	0.0387 (6)
C10	0.3612 (2)	0.52917 (17)	0.38463 (15)	0.0348 (5)
C11	0.4199 (2)	0.58415 (17)	0.32891 (15)	0.0328 (5)
C12	0.5182 (2)	0.54022 (18)	0.28315 (16)	0.0385 (5)
H12	0.557066	0.574331	0.245476	0.046*
C13	0.5552 (2)	0.45072 (19)	0.29359 (17)	0.0441 (6)
H13	0.619162	0.424749	0.262900	0.053*
C14	0.4993 (2)	0.39459 (18)	0.35034 (17)	0.0425 (6)
C15	0.5376 (3)	0.30220 (19)	0.36274 (19)	0.0543 (7)
H15	0.602553	0.275633	0.333924	0.065*
C16	0.4794 (3)	0.2501 (2)	0.4177 (2)	0.0639 (9)
H16	0.504763	0.188080	0.424359	0.077*
C17	0.3854 (3)	0.2885 (2)	0.4621 (2)	0.0594 (8)
H17	0.348171	0.252560	0.499167	0.071*
C18	0.4385 (2)	0.96950 (17)	0.19860 (16)	0.0353 (5)
C19	0.5426 (2)	1.02476 (17)	0.17440 (16)	0.0350 (5)
C20	0.5477 (2)	1.11366 (19)	0.14404 (18)	0.0440 (6)
H20	0.479004	1.147201	0.135935	0.053*
C21	0.6579 (3)	1.1507 (2)	0.12628 (19)	0.0496 (7)
H21	0.664091	1.210943	0.107167	0.059*
C22	0.7592 (3)	1.0996 (2)	0.13645 (19)	0.0493 (7)
H22	0.832437	1.125507	0.123392	0.059*
C23	0.7534 (2)	1.0100 (2)	0.16586 (17)	0.0432 (6)
H23	0.821363	0.975195	0.171883	0.052*
C24	0.6443 (2)	0.97431 (17)	0.18586 (16)	0.0341 (5)
C25	0.6149 (2)	0.87860 (17)	0.21841 (16)	0.0328 (5)
C26	0.6866 (2)	0.88414 (17)	0.31686 (16)	0.0330 (5)
C27	0.6728 (2)	0.95624 (18)	0.40311 (17)	0.0390 (5)
H27	0.614446	1.001430	0.400478	0.047*
C28	0.7411 (2)	0.96405 (19)	0.49217 (17)	0.0397 (6)
H28	0.726249	1.011867	0.548531	0.048*
C29	0.8340 (2)	0.89971 (19)	0.49862 (17)	0.0389 (5)
C30	0.8449 (2)	0.82428 (18)	0.41275 (17)	0.0395 (6)
H30	0.902786	0.778585	0.414547	0.047*
C31	0.7714 (2)	0.81626 (18)	0.32535 (16)	0.0349 (5)
C32	0.7122 (2)	0.71788 (18)	0.15795 (16)	0.0337 (5)
C33	0.7252 (2)	0.61984 (18)	0.08761 (16)	0.0364 (5)

Table 2: (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C34	0.6515 (3)	0.5986 (2)	−0.01249 (19)	0.0559 (8)
H34C[a]	0.704156	0.613667	−0.056513	0.067*
H34D[a]	0.622690	0.525382	−0.036291	0.067*
H34A[b]	0.700541	0.567066	−0.061009	0.067*
H34B[b]	0.582298	0.548644	−0.018017	0.067*
C35B[a]	0.5461 (11)	0.6574 (8)	−0.0178 (7)	0.051 (3)
H35A[a]	0.525230	0.658568	−0.085293	0.061*
H35B[a]	0.478240	0.618897	−0.002934	0.061*
C36	0.5556 (3)	0.7594 (2)	0.04227 (19)	0.0561 (8)
H36C[a]	0.474502	0.776584	0.051593	0.067*
H36D[a]	0.588441	0.804768	0.007688	0.067*
H36A[b]	0.475398	0.729000	0.044953	0.067*
H36B[b]	0.546639	0.823757	0.025963	0.067*
C37	0.6323 (2)	0.78221 (18)	0.14125 (16)	0.0356 (5)
C38	0.7962 (2)	0.55305 (18)	0.11457 (17)	0.0374 (5)
H38	0.841268	0.574905	0.177439	0.045*
C39	0.8090 (2)	0.45141 (18)	0.05553 (17)	0.0387 (5)
H39	0.756906	0.425725	−0.004038	0.046*
C40	0.8906 (2)	0.38986 (17)	0.07941 (16)	0.0343 (5)
C41	0.9908 (2)	0.41401 (17)	0.16859 (16)	0.0349 (5)
C42	1.0533 (2)	0.31640 (18)	0.14716 (17)	0.0349 (5)
C43	1.1511 (2)	0.2904 (2)	0.20137 (19)	0.0452 (6)
H43	1.188825	0.336342	0.260700	0.054*
C44	1.1928 (2)	0.1949 (2)	0.1665 (2)	0.0516 (7)
H44	1.258072	0.176164	0.202710	0.062*
C45	1.1371 (3)	0.1285 (2)	0.0783 (2)	0.0541 (7)
H45	1.165983	0.065040	0.055414	0.065*
C46	1.0384 (2)	0.15332 (19)	0.0218 (2)	0.0483 (6)
H46	1.001742	0.107980	−0.038155	0.058*
C47	0.9974 (2)	0.24822 (18)	0.05879 (17)	0.0374 (5)
C48	0.8183 (3)	0.2421 (2)	−0.07009 (19)	0.0560 (7)
H48A	0.736119	0.251969	−0.060946	0.084*
H48B	0.826361	0.169509	−0.089744	0.084*
H48C	0.838844	0.272131	−0.120077	0.084*
C49	0.9394 (2)	0.4290 (2)	0.26535 (17)	0.0470 (6)
H49A	0.900302	0.491149	0.278579	0.070*
H49B	1.004333	0.434368	0.318139	0.070*
H49C	0.881442	0.370977	0.259610	0.070*
C50	1.0793 (2)	0.50680 (19)	0.1719 (2)	0.0478 (6)
H50A	1.103515	0.497838	0.108649	0.072*
H50B	1.149569	0.512080	0.220199	0.072*
H50C	1.040404	0.568773	0.188964	0.072*
C51	0.8813 (3)	0.9735 (2)	0.67850 (18)	0.0535 (7)
H51A	0.911908	0.944513	0.730610	0.064*
H51B	0.793923	0.971170	0.674970	0.064*
C52	0.9345 (3)	1.0833 (2)	0.7042 (2)	0.0659 (8)
H52A	0.906460	1.112255	0.652271	0.099*
H52B	1.021406	1.086892	0.713027	0.099*
H52C	0.909799	1.121720	0.764033	0.099*
C53	1.0319 (3)	0.8737 (2)	0.58758 (19)	0.0523 (7)
H53A	1.054109	0.860830	0.522558	0.063*
H53B	1.090540	0.927951	0.632296	0.063*
C54	1.0c370 (3)	0.7793 (3)	0.6186 (2)	0.0705 (9)
H54A	0.985192	0.723516	0.570933	0.106*
H54B	1.010217	0.790332	0.681165	0.106*
H54C	1.118949	0.762141	0.624126	0.106*
C35A[b]	0.6075 (9)	0.6884 (5)	−0.0360 (4)	0.0452 (18)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H35C[b]	0.545908	0.664819	−0.094150	0.054*
H35D[b]	0.674172	0.726945	−0.052244	0.054*

[a]Occupancy: 0.415(14), [b]Occupancy: 0.585(14).

6.38 mmol) were dissolved in the condensation agent acetic anhydride (35.0 mL), and the reaction mixture was stirred at 50 °C for 0.5 h. Then, the resulting mixture was put into the refrigerator immediately to stop the reaction. After the solvent was evaporated under reduced pressure, the crude product was purified by silica gel chromatography (CH_2Cl_2/CH_3CH_2OH=20:1 v/v) to obtain the green microcrystalline, compound 2-[(*E*)-2-[9-(2-carboxyphenyl)-6-(diethylamino)-2,3,4,9-tetrahydro-1*H*-xanthen-4-yl]ethenyl]-1,3,3-trimethyl-3*H*-indol-1-ium. Yield: ca. 50%.

The third reaction is an acylation reaction. The green microcrystalline aforementioned intermediate (1.25 g, 2.24 mmol), catalyst PyBOP (1.4 g, 2.79 mmol) and hydrazine hydrate (2.4 mL) were dispersed in CH_2Cl_2 (25 mL). The mixture was stirred at room temperature for 4 h. After the solvent was evaporated under reduced pressure, the crude product was purified by neutral alumina column chromatography (CH_2Cl_2/CH_3CH_2OH=50:1 v/v) to yield yellow powder, named (4′*E*)-2-amino-6′-(diethylamino)-4′-{2-[(2*E*)-1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene]ethylidene}-1′,2,2′,3,3′,4′-hexahydrospiro[isoindole-1,9′-xanthene]-3-one. Yield: ca. 45%.

The last step of the synthetic protocol is as follows: The yellow powder (0.55 g, 0.96 mmol) obtained from the third step and 1-pyrenecarboxaldehyde (0.33 g, 1.44 mmol) were dispersed in ethanol (25 mL) and refluxed for 4 h, during which a yellow powder appeared. The yellow powder was filtered and washed with ethanol to obtain the title compound. Yield: ca. 40%.

The yellow powder (0.05 mmol, 39.2 mg) was dissolved in a methanol/dichloromethane (v/v = 2:1, 15 mL) to evaporate slowly at room temperature. About one week later, yellow block crystals appeared. Yield: ca. 75%.

Experimental details

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

Comment

Pyrene and its derivatives are a class of excellent fluorescent materials with stable chemical properties, long fluorescence lifetimes and high quantum yields, which have been used to construct chemical sensors [8, 9]. In addition, pyrene fluorophore can generate two kinds of fluorescence emission and exciton, which can be used to design many excellent heavy metal ion specific fluorescence probes [10, 11]. Up to now, many fluorescence probes based on pyrene have been designed [12, 13], but most of them are in the visible region. Herein, a potential near-infrared rhodamine derivative compound is reported, which combines pyrene with rhodamine skeleton and has N, O strong coordination atoms.

The asymmetric unit of the title compound only contains a neutral molecule in a closed-ring form. All bond lengths and angles are in the expected ranges [14, 15]. The amide C=O bond distance is 1.216(3) Å, indicative of the keto form of the amide. The bond length of C21–N2 is 1.285(3) Å, which shows the existence of the Schiff base C=N [14]. The xanthene least-square plane and the pyrene least-square plane dihedral angle is 68.6°. The dihedral angle between the aroylhydrozone plane and the pyrene plane is only 26.3°, which indicates that if the title compound coordinates with metals, it may be in the opened-ring form. Due to the large ellipsoid of the C35 atom, it was split into two parts with occupancy of 0.585(12) for C35A and 0.415(14) for C35B, respectively.

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

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