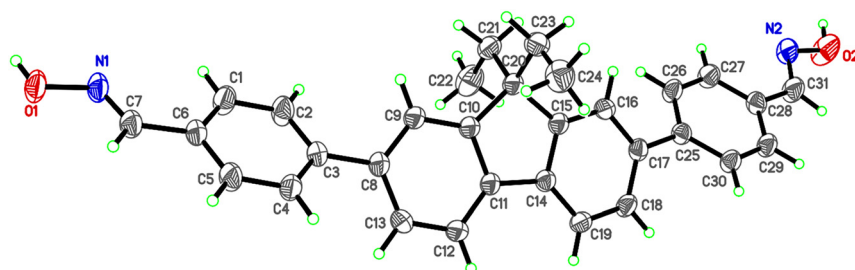


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Crystal structure of (1*E*,1'*E*)-4,4'-(9,9-diethyl-9*H*-fluorene-2,7-diyl)dibenzaldehyde dioxime, C₃₁H₂₈N₂O₂



<https://doi.org/10.1515/ncrs-2023-0385>

Received August 22, 2023; accepted September 27, 2023;

published online October 10, 2023

Abstract

C₃₁H₂₈N₂O₂, triclinic, *P* $\bar{1}$ (no. 2), *a* = 9.0809(9) Å, *b* = 9.2626(9) Å, *c* = 14.8540(15) Å, α = 93.574(8)°, β = 98.554(8)°, γ = 99.558(8)°, *V* = 99.558(8) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0541, *wR*_{ref}(*F*²) = 0.1424, *T* = 293(2) K.

CCDC no.: 2297783

The molecular structure is shown in the figure. Displacement ellipsoids are drawn at the 40 % probability level. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

Raw materials 2,7-dibromo-9,9-diethyl-9*H*-fluorene (3.80 g, 10.0 mmol), 4-formylphenylboronic acid (3.31 g, 22 mmol), K₂CO₃ (8.28 g, 60 mmol) and Pd(PPh₃)₄ (0.76 g, 0.3 mmol) were

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.50 × 0.32 × 0.30 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffraction, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	29.1°, >99 %
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	9746, 5521, 0.025
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2σ(<i>I</i> _{obs}), 3677
<i>N</i> (<i>param</i>) _{refined} :	320
Programs:	Olex2 [1], SHELX [2, 3]

introduced into 100 mL three-necked flask and degassed for three times. The mixture solution of toluene, ethanol and H₂O (3:2:1, v/v/v 80 mL) was slowly added under N₂ atmosphere. The mixture was stirred and refluxed under N₂. The progress of reaction was monitored by thin-layer chromatography. After 40 h, the organic phase was evaporated under vacuum. The residue was purified by column chromatography with dichloromethane/petroleum ether (1:1 v/v) as eluent. The intermediate 4,4'-(9,9-diethyl-9*H*-fluorene-2,7-diyl)dibenzaldehyde was obtained as a light yellow powder.

The intermediate (0.431 g, 1 mmol) and hydroxylamine hydrochloride (0.139 g, 2 mmol) were dissolved in anhydrous methanol (20 mL). Two drops of triethylamine was added to the above solution as a catalyst. The mixture solution was refluxed for 4 h (monitored by TLC). When the reaction is complete, light gray precipitates were filtered and washed with cold methanol. The crystals of the title compound were grown by slow evaporation of its methanol/dichloromethane solution at room temperature.

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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}
O1	0.95431 (17)	0.34140 (16)	0.41397 (9)	0.0538 (4)
H1	1.016939	0.329062	0.457292	0.081*
O2	0.8604 (3)	−1.4046 (2)	−0.64363 (11)	0.0854 (6)
H2	0.901996	−1.467785	−0.619567	0.128*
N1	0.94996 (19)	0.23455 (18)	0.34110 (10)	0.0455 (4)
N2	0.8489 (2)	−1.29613 (19)	−0.57669 (11)	0.0505 (4)
C1	0.8971 (2)	0.0298 (2)	0.18022 (13)	0.0497 (5)
H1A	0.968374	0.011979	0.228069	0.060*
C2	0.8699 (2)	−0.0590 (2)	0.09905 (13)	0.0495 (5)
H2A	0.923299	−0.135602	0.093451	0.059*
C3	0.7643 (2)	−0.0363 (2)	0.02539 (12)	0.0392 (4)
C4	0.6877 (2)	0.0798 (2)	0.03721 (13)	0.0476 (5)
H4	0.617453	0.098946	−0.010806	0.057*
C5	0.7135 (2)	0.1674 (2)	0.11862 (13)	0.0505 (5)
H5	0.658762	0.242766	0.124802	0.061*
C6	0.8196 (2)	0.1450 (2)	0.19135 (12)	0.0400 (4)
C7	0.8469 (2)	0.2444 (2)	0.27519 (13)	0.0446 (5)
H7	0.787393	0.316246	0.280171	0.053*
C8	0.7342 (2)	−0.1327 (2)	−0.06144 (12)	0.0390 (4)
C9	0.7321 (2)	−0.2835 (2)	−0.06069 (12)	0.0398 (4)
H9	0.747484	−0.324380	−0.005177	0.048*
C10	0.7074 (2)	−0.3730 (2)	−0.14132 (11)	0.0366 (4)
C11	0.6874 (2)	−0.3118 (2)	−0.22579 (11)	0.0354 (4)
C12	0.6862 (2)	−0.1626 (2)	−0.22743 (12)	0.0426 (5)
H12	0.670435	−0.121764	−0.282926	0.051*
C13	0.7086 (2)	−0.0745 (2)	−0.14595 (13)	0.0444 (5)
H13	0.706498	0.025345	−0.147455	0.053*
C14	0.67471 (19)	−0.42972 (19)	−0.29884 (11)	0.0344 (4)
C15	0.68186 (19)	−0.5615 (2)	−0.25867 (11)	0.0347 (4)
C16	0.6827 (2)	−0.6894 (2)	−0.31057 (11)	0.0374 (4)
H16	0.685650	−0.776398	−0.282822	0.045*
C17	0.67916 (19)	−0.6891 (2)	−0.40501 (11)	0.0350 (4)
C18	0.6680 (2)	−0.5578 (2)	−0.44492 (12)	0.0395 (4)
H18	0.662138	−0.557004	−0.507926	0.047*
C19	0.6655 (2)	−0.4286 (2)	−0.39318 (12)	0.0392 (4)
H19	0.657710	−0.342482	−0.421102	0.047*
C20	0.6987 (2)	−0.5385 (2)	−0.15493 (11)	0.0373 (4)
C21	0.8424 (2)	−0.5888 (2)	−0.10902 (13)	0.0498 (5)
H21A	0.853585	−0.565556	−0.043512	0.060*
H21B	0.829584	−0.694816	−0.120295	0.060*
C22	0.9865 (3)	−0.5198 (3)	−0.14161 (16)	0.0681 (7)
H22A	0.977213	−0.542955	−0.206335	0.102*
H22B	1.070648	−0.557678	−0.110776	0.102*
H22C	1.002842	−0.415054	−0.128321	0.102*
C23	0.5595 (2)	−0.6226 (2)	−0.12067 (13)	0.0488 (5)
H23A	0.550497	−0.726523	−0.138796	0.059*
H23B	0.576579	−0.610095	−0.054397	0.059*
C24	0.4117 (3)	−0.5753 (3)	−0.15540 (16)	0.0612 (6)
H24A	0.403517	−0.566857	−0.219968	0.092*
H24B	0.408392	−0.481869	−0.124638	0.092*
H24C	0.329117	−0.647002	−0.143683	0.092*
C25	0.69764 (19)	−0.8232 (2)	−0.45854 (11)	0.0353 (4)
C26	0.7939 (2)	−0.9130 (2)	−0.42002 (12)	0.0420 (5)
H26	0.843610	−0.888367	−0.360266	0.050*
C27	0.8180 (2)	−1.0369 (2)	−0.46732 (13)	0.0462 (5)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H27	0.883256	−1.094308	−0.439487	0.055*
C28	0.7449 (2)	−1.0768 (2)	−0.55685 (12)	0.0407 (4)
C29	0.6485 (2)	−0.9883 (2)	−0.59586 (12)	0.0425 (5)
H29	0.598771	−1.013409	−0.655560	0.051*
C30	0.6246 (2)	−0.8635 (2)	−0.54820 (12)	0.0396 (4)
H30	0.559291	−0.806111	−0.576092	0.047*
C31	0.7709 (3)	−1.2050 (2)	−0.61017 (14)	0.0538 (6)
H31	0.728291	−1.220746	−0.671662	0.065*

2 Experimental details

Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program and refined with the SHELXL [3] refinement package. The C-bound H atoms were geometrically placed (C–H = 0.93–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The O-bound H atom was located in a difference map and refined with O–H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

3 Comment

Fluorene and its derivatives have drawn much attention because of their wide variety of application in photophysics and photochemistry [4–6]. This unique structure leads to the result that fluorene segment are rigidly coplanar with the delocalized π -conjugated system. Simultaneously, the five-membered ring (C-9 position) and two benzene rings are easily modified by some functional groups and/or solubilizing groups. The functional structures make fluorene compounds showing high photoluminescence quantum yields, thermal stabilities and good solubility in water [7, 8]. However, the short excitation and emission wavelengths of fluorene dyes limit their wide applications in biological systems [9]. In order to solve this problem, it is important that the π -bridge conjugated systems of fluorene compounds will be extended by the structural modification [10]. Suitable substitutions can not only enhance the intensities of their absorption and emission peaks but also produce a red shift. Based on the above considerations, the title compound containing fluorene moiety and aromatic rings was synthesized by SUZUKI couple and Schiff base reaction [11].

X-ray single crystal diffraction analysis reveals that the title compound crystallizes in the triclinic space group $P\bar{1}$ with one independent molecule in the asymmetric unit (*cf.* the figure). In the molecular structure, the bond lengths of C7–N1 and C31–N2 are 1.269(2) and 1.268(3) Å, respectively,

which belong to the typical C=N double bonds. Other bond lengths and bond angles are all in the normal ranges [12–14]. The groups C6–C7–N1–O1 and C28–C31–N2–O2 exhibit similar torsion angles with the value of $-179.90(17)^\circ$ and $-177.6(2)^\circ$, respectively. According to the values of the torsion angles, it was found that the title compound adopts *E,E'* configurations. In the title compound, the benzene rings in the fluorene fragment are almost coplanar with the dihedral angle of $5.75(4)^\circ$. Moreover, the aromatic rings are rotated relative to the fluorene segment with the dihedral angles between the aromatic ring and adjacent benzene ring of the fluorene moiety being $36.55(7)^\circ$ and $39.04(8)^\circ$, respectively. Like most discrete organic molecules, hydrogen bond interactions play an important role in the self-assemble. In the crystal, adjacent molecules are linked to form one dimensional chain by O2–H2...O1 hydrogen bonds (H2...O1 = 1.9788(2) Å). The neighboring chains further interact with each other via π – π interactions to construct a double chain structure [centroid-to-centroid distance between the two C25–C26–C27–C28–C29–C30 rings = 4.0155(4) Å] along the *a* axis. Adjacent double chains are connected to form two dimensional layer structure through O1–H1...N2 hydrogen bonds (O1–H1...N2 = 2.0666(2) Å).

In the title compound, the oxime functional group could be chosen as a highly selective recognition group for ClO^- . Previous results have shown that the oxime can be oxidized into aldehyde group [15, 16]. The corresponding fluorescence intensity and position will undergo significant changes.

Research ethics: This work don't involve research ethics.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Competing interests: The authors declare no conflicts of interest regarding this article.

Research funding: This work was supported by the Project of the Shandong Province Higher Educational Science and Technology Program (No. J18KA092).

Data availability: All relevant data are within the paper and its Supporting Information files.

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