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Crystal structure of 3-(diethylamino)-7,9,11-trimethyl-8-phenyl-6*H*,13*H*-12λ^4,13λ^4-chromeno[3′,4′:4,5]pyrrolo[1,2-*c*]pyrrolo[2,1-*f*][1,3,2]diazaborinin-6-one, $C_{28}H_{26}BF_2N_3O_2$

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Abstract

$C_{28}H_{26}BF_2N_3O_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.134(4) Å, b = 9.932(2) Å, c = 15.420(4) Å, α = 73.607(13)°, β = 75.010(14)°, γ = 63.294(14)°, V = 1184.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.0423, $wR_{ref}(F^2)$ = 0.1292, T = 303 K.

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The molecular structure is shown in the Figure 1. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of material

The title compound, 3-(diethylamino)-7,9,11-trimethyl-8-phenyl-6*H*,13*H*-12λ^4,13λ^4-chromeno[3′,4′:4,5]pyrrolo[1,2-*c*]pyrrolo[2,1-*f*][1,3,2]diazaborinin-6-one, was synthesized according to the literature method with a slight modification.[6] Under the argon atmosphere, 2-benzoylchromeno[4,3-*b*]pyrrol-4(1*H*)-one (650 mg, 1.8 mmol) was charged in a dry three-neck flask and mixed with dichloromethane (130 mL), 2,4-dimethylpyrrole (0.18 mL, 1.8 mmol), and phosphoryl chloride (0.17 mL, 1.8 mmol). The reaction mixture was stirred at room temperature for about 3 days. The reaction progress was monitored by thin-layer chromatography (TLC). When the TLC analysis indicated the complete consumption of 2-benzoylchromeno[4,3-*b*]pyrrol-4(1*H*)-one, triethylamine (2.5 mL) was added and stirring the mixture continuously for 15 min. Then, boron trifluoride etherate ($BF_3{\cdot}Et_2O$, 2.5 mL) was added and the reaction mixture was stirred furtherly for more than 8 h at room temperature. The solution color turned to red. The mixture was quenched with

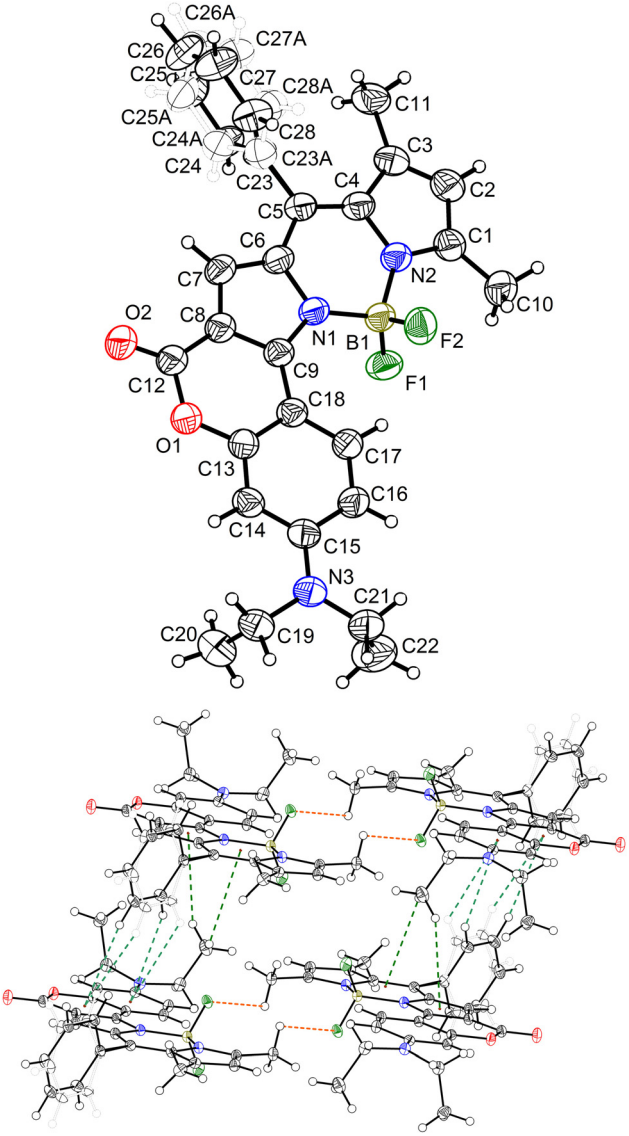

Figure 1: A view of the molecule. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radii.

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Table 1: Data collection and handling.

Crystal:	Clear reddish black block
Size:	0.18 × 0.15 × 0.13 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, ω scans
θ_{max}, completeness:	29.5°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	53008, 6517, 0.055
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4,823
$N(param)_{refined}$:	384
Programs:	Bruker,[1] SHELX,[2–4] Olex2[5]

distilled water (50 mL) and then it was extracted with dichloromethane (50 mL × 3), washed with distilled water (50 mL × 3). The collected organic phase was dried over $MgSO_4$. The volatile component was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh), using dichloromethane as the eluent. The crystal growth was carried in saturated dichloromethane/methanol (10:1) and the solution sealed in a 10 mL vial with parafilm. The number of holes on the parafilm was used to control the solvent evaporation speed. Finally, regular shaped crystals can be obtained and mounted for X-ray diffraction.

2 Experimental details

The single-crystal X-ray diffraction measurement of the title compound, 3-(diethylamino)-7,9,11-trimethyl-8-phenyl-6*H*,13*H*-12λ^4,13λ^4-chromeno[3′,4′:4,5]pyrrolo[1,2-*c*]pyrrolo[2,1-*f*][1,3,2]diazaborinin-6-one, was carried out on a Bruker D8 Venture. Data reduction was carried out using Appex5 and empirical absorption corrections were made using SADABS-2016/2. The structure was solved by using the programs of SHELX and refined by ShelXl through the Olex2 interface.[1–4] Hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, assigned isotropic thermal parameters with *d*(C–H) = 0.93, 0.96 or 0.97 Å (–CH, $–CH_3$, and $–CH_2$). U_{iso}(H) = 1.2U_{eq}(C) for CH and U_{iso}(H) = 1.5U_{eq}(C) for CH_3 and CH_2 groups.[2] The benzene ring (C23/C24/C25/C26/C27/C28) attached at the **meso**-position of BODIPY was disordered due to the rotation around the single bond (C5–C23). Therefore, it was split to two parts with 54 % and 46 %, respectively. SAME and SIMU command were used to restrict the two disordered benzene rings to maintain regular geometry configuration. No other constraints or restraints were used in further data refining. The molecular graphics were drawn using DIAMOND software with 50 % probability ellipsoids in the figure (top).

3 Comment

The structure of the title compound incorporates the typical fluorescent coumarin and BODIPY (4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene) both. It combines the photocharacter of two fluorophores and broadens the application in fluorescent sensors, fluorescent labeling of biomolecules and cells, photodynamic therapy, and light-emitting materials, etc.[7–11] The crystal structure demonstrates that the coumarin moiety fused with that of the BODIPY part and a significant red-shift in fluorescent emission maximum. The conjugate electron cloud could be delocalized to both coumarin and BODIPY part, which endows its unique character in fluorescent emission.[6]

In the title crystal structure, the asymmetric unit contains only one molecules. The BODIPY part is coplanar with the RMSD in distance estimated to be 0.032 Å. However, the BODIPY and coumarin fused together through C8–C9 (1.408 Å), which is slightly longer than that of the classical carbon–carbon double bond (1.339 Å) and has the partial character of double bond. Therefore, the whole part of coumarin-BODIPY part fused by the partially π character of C8–C9 also becomes planarization with the RMSD 0.052 Å. This large conjugate system leads to a strong absorption shift toward the longer wavelength (around 600 nm). In addition, the bond length of N3–C15 is 1.365 Å, which is shorter than that of N3–C19 (1.463 Å) and N3–C21 (1.455 Å). It demonstrates that the electron rich N3 conjugated with the coumarin ring, which can effectively donate the electron toward the coumarin and BODIPY moiety. The electron donor (NEt_2) and carbonyl group (C12/O2) configures a strong intramolecular electron "push–pull" effect, which determines the emission performance of coumarin-/BODIPY-containing dyes.[12–15] Additionally, the configuration of amino (N3/C15/C19/C21) does not construct the ideal trigonal pyramid geometry but coplanar with the RMSD 0.042 Å. It indicates that the lone pair electron of N3 partial involved in the bond formation of N3–C15 and leads to its partial π character, showing the electron donation of N3 to coumarin ring. The adjacent parallel molecules are fixed by the C–H···π interactions (figure bottom). The hydrogen atoms (H27/H27A/H28/H28A/H22A/H22C) locate directly above the carbon ring. The H···centroid distance ranged from 2.95 to 3.45 Å, which is well inside the interval 2.65 to 4.0 Å.[16] The C–H bonds point to the ring carbon rings center and corresponds to the type III geometry. In addition, typical C–H···O interactions are also found in the crystal. The C···O distances are 3.455 and 3.834 Å (C14···O2 and C19···O2). The hydrogen bonds configuration in the crystal is significant to uncover the principle of the solid emission behavior of the fluorescent

dyes.[17–20] Therefore, reasonable introduction of inter- and/or intra-molecular hydrogen bonds into the crystal lattice is an effective methodology to inhibit the ration of non-radiative channels.[21,22] The existence of heteroatom O/N/S is key to configure intermolecular hydrogen bonds.[23–25] When there exist highly stronger intermolecular interactions, a significant emission quench will be unavoided.[26–28]

The related crystal structures are mainly stabilized by the hydrogen bonds and C–H$\cdots\pi$ interactions. The hydrogen bonds join the adjacent molecules side by side. The hydrogen bond join the paralleled molecules to form the network.[29–31] Generally, the stronger hydrogen bonds are the determining factor to the optical properties of the compound in crystal state.[32,33] Therefore, it is important that the heteroatoms involved hydrogen bonds are key to the optical properties.[34–36] Both the bond lengths and the angles are in the expected ranges.

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