Yingfan Liu* and Zhiqiang Zhao

Crystal structure of (*Z*)-2-(*tert*-butyl)-5-((5-(*tert*-butyl)-2*H*-pyrrol-2-ylidene)(mesityl)methyl)-1*H*-pyrrole, $C_{26}H_{34}N_2$

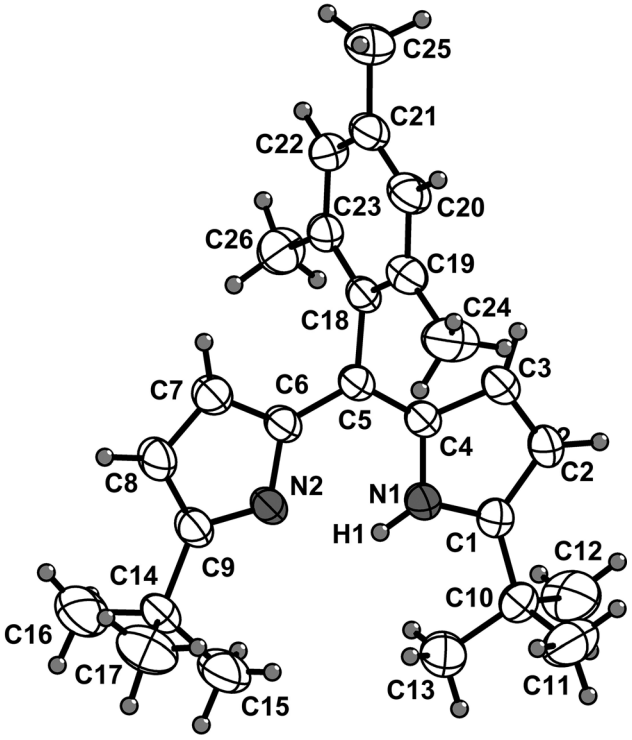

Figure 1: A view of the molecule. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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Abstract

$C_{26}H_{34}N_2$, orthorhombic, *Pbca* (no. 61), a = 14.8062(2) Å, b = 15.8918(2) Å, c = 20.0121(3) Å, V = 4708.79(11) Å^3, Z = 8, $R_{gt}(F)$ = 0.0548, $wR_{ref}(F^2)$ = 0.1701, T = 296.2 K.

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***Corresponding author: Yingfan Liu**, College of Material and Chemical Engineering, Zhengzhou University of Light Industry, Henan Provincial Key Lab of Surface and Interface Science, Zhengzhou 450002, P. R. China, E-mail: yfliu@zzuli.edu.cn

Zhiqiang Zhao, College of Material and Chemical Engineering, Zhengzhou University of Light Industry, Henan Provincial Key Lab of Surface and Interface Science, Zhengzhou 450002, P. R. China

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.40 × 0.25 × 0.20 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	0.46 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	66.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8907, 4155, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3592
$N(param)_{refined}$:	298
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

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

Source of material

The title compound, (*Z*)-2-(*tert*-butyl)-5-((5-(*tert*-butyl)-2*H*-pyrrol-2-ylidene)(mesityl)methyl)-1*H*-pyrrole, was synthesized according to the literatured methodology [5, 6]. The synthesis includes two step of synthesis and seperation. Due to the tedious work-up procedure, we modified the synthetic procedure of the title compound to a one pot reaction. Firstly the 2,4,6-trimethylbenzaldehyde (296 mg, 2 mmol) was dissolved in anhydrous dichloromethane (60 mL) under nitrogen atmosphere. Then 2-*tert*-butylpyrrole (492 mg, 4 mmol) and trifluoroacetic acid (one drop) were added by syringe successively. The solution was stirred at room temperature for 5 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 495 mg, 2 mmol) in dichloromethane (10 mL) was added to the reaction mixture and stirred at room temperature continuously for about 1 h. The reaction progress was monitored by TLC. Once the starting material 2,4,6-trimethylbenzaldehyde disappeared totally and the target spot formed regularly, the reaction mixture was quenched by adding 100 mL distilled water. Then, a successive extraction, washing, and drying over anhydrous $MgSO_4$ was done. The seperated organic phase was concentrated and removed in vacuum. The resulting cruded product was purified by

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.52466 (11)	0.28852 (10)	0.58026 (9)	0.0555 (4)
C2	0.60593 (12)	0.24062 (11)	0.57549 (11)	0.0673 (5)
H2	0.610364	0.183953	0.564378	0.081*
C3	0.67571 (11)	0.29312 (10)	0.59020 (10)	0.0623 (4)
H3	0.736728	0.279259	0.590705	0.075*
C4	0.63775 (10)	0.37299 (9)	0.60463 (9)	0.0533 (4)
C5	0.68041 (10)	0.44658 (9)	0.62482 (8)	0.0507 (4)
C6	0.63472 (10)	0.52193 (10)	0.64032 (8)	0.0531 (4)
C7	0.66921 (11)	0.59968 (11)	0.66177 (10)	0.0632 (5)
H7	0.729647	0.612591	0.669203	0.076*
C8	0.59701 (12)	0.65320 (11)	0.66976 (11)	0.0679 (5)
H8	0.599879	0.709114	0.683296	0.081*
C9	0.51827 (11)	0.60839 (10)	0.65383 (9)	0.0573 (4)
C10	0.42905 (11)	0.25767 (11)	0.57144 (10)	0.0622 (4)
C11	0.40300 (17)	0.21140 (19)	0.63540 (14)	0.1021 (8)
H11A	0.444994	0.166476	0.643331	0.153*
H11B	0.343241	0.188699	0.630776	0.153*
H11C	0.404367	0.249928	0.672335	0.153*
C12	0.42317 (17)	0.19595 (19)	0.51390 (15)	0.1060 (9)
H12A	0.436326	0.224554	0.472781	0.159*
H12B	0.363368	0.172748	0.511901	0.159*
H12C	0.466088	0.151455	0.520552	0.159*
C13	0.36484 (14)	0.33030 (15)	0.56057 (18)	0.1059 (9)
H13A	0.369991	0.369275	0.597019	0.159*
H13B	0.304055	0.309474	0.558270	0.159*
H13C	0.379672	0.358300	0.519499	0.159*
C14	0.42112 (11)	0.63734 (11)	0.65556 (10)	0.0651 (5)
C15[a]	0.3560 (2)	0.5660 (3)	0.6393 (3)	0.1149 (15)
H15A[a]	0.295005	0.586189	0.642424	0.172*
H15B[a]	0.364666	0.520811	0.670440	0.172*
H15C[a]	0.367217	0.546166	0.594759	0.172*
C16[a]	0.4091 (4)	0.7125 (4)	0.6153 (3)	0.1174 (16)
H16A[a]	0.349997	0.735386	0.623092	0.176*
H16B[a]	0.415266	0.698385	0.568859	0.176*
H16C[a]	0.453945	0.753397	0.627247	0.176*
C17[a]	0.3989 (3)	0.6597 (4)	0.7304 (2)	0.1071 (12)
H17A[a]	0.435861	0.706073	0.744460	0.161*
H17B[a]	0.411064	0.611742	0.758191	0.161*
H17C[a]	0.336394	0.674825	0.734211	0.161*
C18	0.78122 (10)	0.44651 (9)	0.63274 (8)	0.0492 (4)
C19	0.81994 (11)	0.41134 (11)	0.69009 (8)	0.0583 (4)
C20	0.91302 (11)	0.41580 (12)	0.69813 (10)	0.0637 (5)
H20	0.938919	0.392233	0.736103	0.076*
C21	0.96828 (11)	0.45396 (10)	0.65172 (10)	0.0610 (4)
C22	0.92876 (11)	0.48623 (10)	0.59463 (9)	0.0589 (4)
H22	0.965293	0.510874	0.562283	0.071*
C23	0.83599 (10)	0.48293 (9)	0.58415 (8)	0.0517 (4)
C24	0.76315 (14)	0.37023 (17)	0.74355 (11)	0.0906 (7)
H24A	0.793851	0.373839	0.785706	0.136*
H24B	0.753473	0.312193	0.732342	0.136*
H24C	0.706013	0.398526	0.746605	0.136*
C25	1.06853 (13)	0.46107 (15)	0.66407 (15)	0.0896 (7)
H25A	1.093705	0.502714	0.634740	0.134*
H25B	1.096740	0.407707	0.655703	0.134*
H25C	1.078917	0.477297	0.709636	0.134*
C26	0.79699 (14)	0.51802 (13)	0.52054 (10)	0.0747 (5)
H26A	0.761443	0.475565	0.498795	0.112*
H26B	0.845131	0.535289	0.491482	0.112*
H26C	0.759503	0.565602	0.530770	0.112*
N1	0.54405 (9)	0.36660 (8)	0.59755 (7)	0.0539 (3)
N2	0.54158 (9)	0.53041 (8)	0.63599 (7)	0.0547 (4)
H2A[b]	0.504708	0.491540	0.623752	0.066*
H1[c]	0.508 (2)	0.4088 (19)	0.600 (2)	0.067 (14)*
C15A[d]	0.3787 (4)	0.6158 (6)	0.5844 (4)	0.098 (2)
H15D[d]	0.314012	0.619234	0.586916	0.148*
H15E[d]	0.395949	0.559848	0.571504	0.148*
H15F[d]	0.400423	0.655238	0.551819	0.148*
C16A[d]	0.4166 (6)	0.7334 (4)	0.6600 (6)	0.111 (3)
H16D[d]	0.446273	0.757560	0.621880	0.167*
H16E[d]	0.446164	0.751847	0.700085	0.167*
H16F[d]	0.354611	0.750998	0.660742	0.167*
C17A[d]	0.3723 (5)	0.5968 (7)	0.7073 (5)	0.117 (3)
H17D[d]	0.375589	0.630055	0.747247	0.175*
H17E[d]	0.397992	0.542333	0.715480	0.175*
H17F[d]	0.310340	0.590659	0.694074	0.175*

[a]Occupancy: 0.65, [b]Occupancy: 0.52(3), [c]Occupancy: 0.48(3), [d]Occupancy: 0.35.

column chromatography, yielding a yellow powder. Crystals were obtained by slow evaporation its solution in dichloromethane within several days.

Experimental details

The hydrogen atoms were placed in geometrically positions and refined using a riding model with *d*(C—H) = 0.93 Å(aromatic), 0.96 Å(–C*H*$_3$), 0.86 Å(–N*H*). U_{iso}(H) = 1.2 U_{eq}(C) for CH or U_{iso}(H) = 1.5 U_{eq}(C) for CH_3 and NH groups [3]. One of the tertiary butyl, attached to the *α* position of pyrrole ring, is disordered. The disordered two parts were processed by rotating around the axis of C9—C14 with site occupation 0.65 and 0.35, respectively (not shown in the figure). In addition, the hydrogen atom attached to N1 was also treated as disordered atom due to the symmetric-plane. The H2A, part 2, was assigned to N2 with site occupation 0.52.

Comment

When we configure the dipyrrin metal complexes, the dipyrrin derivatives will be the important ligands [7–9]. Up to now, many metals have been involved in the dipyrrin related complexes, such as Zn, Fe, Sn, Cu, B etc. [7]. Among various dipyrrin complexes, the F–B dipyrrin complexes

attracted the attention due to their strong fluorescence emission [10–15]. With fine tuning the structure of dipyrrin F–B complexes, the emission wavelength can be significantly shifted according to the material requirement.

In the title crystal structure, the asymmetric unit contains on molecules. Both the bond lengths and the angles are in the expected ranges. The two pyrrole rings were connected by C5 and configured a plane with the RMSD estimated to be 0.021 Å. In fact, the two pyrrole rings are conjugated. The distance of C4—C5 and C5—C6 are 1.389 and 1.410 Å, respectively, which has the character of double and single bond. Together with the analysis of bond length of the two pyrrole rings, alternating single/double bond was observed in the plane (C1/C2/C3/C4/N1/C5/C6/C7/C8/C9/N2), supporting the regular aromaticity. In addition, the plane also was stabilized by the intramolecular hydrogen bond (N1—H1···N2) and (N2—H2A···N1). The H···O distance was estimated to be 2.124 and 2.135 Å. The N1···N2 contact was 2.715 Å, which is inside the interval of 3.0–4.0 Å, basing on a survey of over 100 structures. The N—H···N angles (125.5 and 124.4°) are also in agreement with the literature [16, 17]. According to the structural analysis, only one hydrogen atom is attached to the nitrogen atom. However, the electron density around N2 indicates that part of the hydrogen atom bonded to N2. This kind of hydrogen disorder can also be found in other dipyrrin derivatives [6, 18, 19]. Once the two nitrogen atoms were protonated both, the plane involving two pyrrole rings will be significant twisted [8, 20]. The distance between C5—C18 is determined to be 1.501 Å, and can be characterized as a single bond. At the same time, the highly hindered methyl (C24/C26) groups at the mesity moiety (C18/C19/C20/C21/C22/C23) twist away with respect to the two pyrrole configured plane with the torsion angle of 78.2°. In solution or solid state, the rotating restriction of meso-substituted benzene ring contributes to the emission of dipyrrin complexes in a certain degree.

The intermolecular interactions that stabilized the crystal lattice are C—H···π interactions. The hydrogen atoms (H13C, H25C, H15F etc.) located directly above the pyrrole or benzene ring stabilizes the adjacent molecules in layers [21]. Also, the hydrogen bonds and C—H···π interactions constructs the crystal network. It is important for us to understand the emission behavior of dipyrrin dyes in aggregate states. Both the emission enhancement or quenching of dye depends on various intermolecular interaction [22, 23].

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

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