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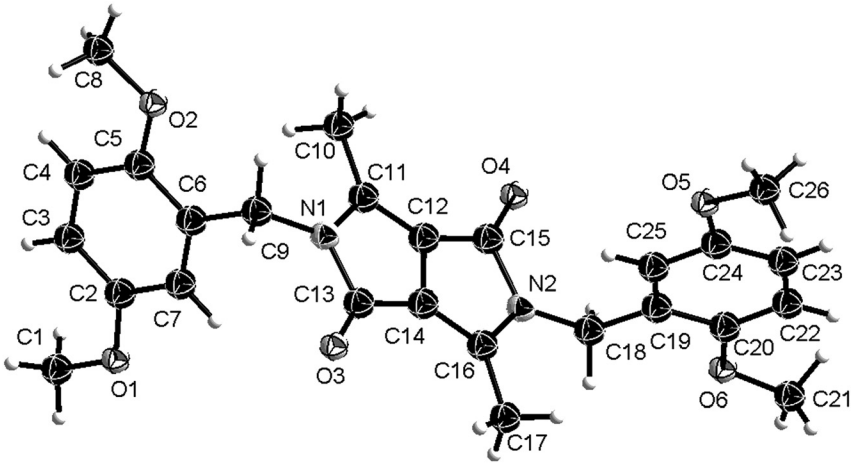
Crystal structure of 2,5-bis(2,5-dimethoxybenzyl)-3,6-dimethyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, $C_{26}H_{28}N_2O_6$



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Abstract

$C_{26}H_{28}N_2O_6$, monoclinic, $P2_1/c$ (no. 14), a = 15.962(9) Å, b = 14.828(8) Å, c = 9.929(5) Å, β = 93.303°, V = 2346(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0515, w$R_{ref}(F^2)$ = 0.1621, T = 296(2) K.

CCDC no.: 2339004

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.

Table 1: Data collection and handling.

Crystal:	Yellow needle
Size:	0.10 × 0.05 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25,898, 5290, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3316
$N(param)_{refined}$:	313
Programs:	Bruker,1 SHELX[2]

1 Source of material

A dichloromethane (12 mL) solution of (2,5-dimethoxyphenyl) methanamine (1.0 g, 6 mmol) and triethylamine (0.03 mL, 8 mmol) was added to a 50 ml round bottom flask and cooled to 0 °C. At this temperature, fumaric chloride (0.7 ml, 4 mmol) in dichloromethane (6 mL) was added drop by drop within 1 h, and white smoke was observed, and a large amount of white precipitation was observed in the reaction mixture. After removing the ice bath, reaction mixture was stirred at room temperature overnight. After the reaction was completed, the solution was filtered first, and the obtained

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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	0.40194 (9)	0.43814 (12)	0.38300 (16)	0.0931 (5)
O2	0.46942 (9)	0.34548 (12)	−0.13755 (15)	0.0847 (5)
O3	0.71889 (8)	0.47381 (9)	0.23339 (14)	0.0663 (4)
O4	0.77020 (8)	0.08449 (9)	0.33455 (14)	0.0649 (4)
O5	1.07840 (9)	0.17698 (12)	0.16670 (14)	0.0911 (5)
O6	1.00535 (8)	0.09394 (9)	0.68705 (13)	0.0666 (4)
N1	0.66014 (8)	0.34255 (10)	0.13973 (14)	0.0499 (4)
N2	0.82677 (8)	0.21630 (9)	0.42968 (14)	0.0491 (4)
C1	0.31991 (16)	0.4364 (2)	0.4280 (3)	0.1002 (8)
H1A	0.284725	0.476076	0.373233	0.150*
H1B	0.320889	0.455964	0.520308	0.150*
H1C	0.298174	0.376145	0.421298	0.150*
C2	0.41217 (12)	0.41349 (13)	0.2511 (2)	0.0622 (5)
C3	0.34777 (12)	0.39277 (13)	0.1581 (2)	0.0676 (6)
H3	0.292457	0.394701	0.182641	0.081*
C4	0.36530 (12)	0.36927 (13)	0.0290 (2)	0.0680 (6)
H4	0.321518	0.354623	−0.032984	0.082*
C5	0.44699 (11)	0.36701 (13)	−0.01047 (19)	0.0569 (5)
C6	0.51281 (10)	0.38739 (11)	0.08316 (18)	0.0511 (4)
C7	0.49396 (11)	0.41034 (13)	0.21263 (19)	0.0585 (5)
H7	0.537443	0.424040	0.275689	0.070*
C8	0.40582 (16)	0.3354 (2)	−0.2396 (3)	0.1031 (9)
H8A	0.430248	0.319873	−0.322599	0.155*
H8B	0.375455	0.391061	−0.250907	0.155*
H8C	0.368149	0.288476	−0.215229	0.155*
C9	0.60201 (10)	0.38637 (13)	0.04114 (18)	0.0564 (5)
H9A	0.603871	0.355180	−0.044514	0.068*
H9B	0.620305	0.447951	0.027873	0.068*
C10	0.61561 (12)	0.18480 (14)	0.0795 (2)	0.0649 (5)
H10A	0.557432	0.200249	0.084018	0.097*
H10B	0.625008	0.125237	0.115120	0.097*
H10C	0.630585	0.186481	−0.012750	0.097*
C11	0.66760 (10)	0.25007 (11)	0.15955 (17)	0.0473 (4)
C12	0.72822 (10)	0.23661 (11)	0.26063 (17)	0.0469 (4)
C13	0.71545 (10)	0.39170 (12)	0.23009 (17)	0.0486 (4)
C14	0.75946 (10)	0.32170 (11)	0.30726 (16)	0.0460 (4)
C15	0.77246 (10)	0.16676 (12)	0.33795 (17)	0.0481 (4)
C16	0.81921 (10)	0.30892 (11)	0.40929 (17)	0.0474 (4)
C17	0.86911 (12)	0.37555 (14)	0.4898 (2)	0.0674 (5)
H17A	0.847157	0.380979	0.577426	0.101*
H17B	0.866155	0.432987	0.445148	0.101*
H17C	0.926499	0.356047	0.499182	0.101*
C18	0.88477 (11)	0.17168 (13)	0.52602 (17)	0.0543 (5)
H18A	0.860236	0.114934	0.552262	0.065*
H18B	0.891770	0.208914	0.606204	0.065*
C19	0.97001 (10)	0.15318 (11)	0.47421 (17)	0.0483 (4)
C20	1.03000 (11)	0.11051 (11)	0.55933 (18)	0.0501 (4)
C21	1.06607 (16)	0.05861 (18)	0.7816 (2)	0.0944 (8)
H21A	1.087992	0.003348	0.747575	0.142*
H21B	1.040674	0.047116	0.865211	0.142*
H21C	1.110857	0.101328	0.796302	0.142*
C22	1.10663 (11)	0.08756 (12)	0.5126 (2)	0.0590 (5)
H22	1.146015	0.057825	0.569160	0.071*
C23	1.12558 (11)	0.10849 (13)	0.3814 (2)	0.0613 (5)
H23	1.177317	0.092466	0.350057	0.074*
C24	1.06742 (11)	0.15307 (13)	0.29799 (19)	0.0596 (5)
C25	0.99014 (11)	0.17481 (13)	0.34516 (18)	0.0578 (5)
H25	0.950901	0.204698	0.288477	0.069*
C26	1.15943 (15)	0.17291 (18)	0.1203 (2)	0.0905 (7)
H26A	1.159134	0.197260	0.030737	0.136*
H26B	1.177801	0.111273	0.119309	0.136*
H26C	1.196975	0.207395	0.179190	0.136*

white solid was washed with sodium hydroxide (1 mol/L) and hydrochloric acid (1 mol/L) with cold dichloromethane. After vacuum drying, the product N^1,N^4-bis(2,5-dimethoxybenzyl) fumaramide (1.24 g, 3 mmol) was obtained as a white solid. Compound N^1,N^4-bis(2,5-dimethoxybenzyl)fumaramide (8.284 g, 20 mmol) and isopropyl acetate (150 mL) were added to a 500 mL round bottom flask. Then a dimethylformamide solution of p-toluenesulfonic acid (20 mL, 0.10 mol/L) was added, and the reaction mixture was heated at 105 °C (oil bath) in a nitrogen atmosphere, stirring for 12 h. It was observed that the white solid gradually dissolved, and the solution turned brown and yellow. After the reaction, it was cooled to room temperature, and the reaction mixture was concentrated under reduced pressure to remove most of the solution. The residue was dissolved in ethyl acetate (300 mL) and washed by 5 % HCl aqueous solution (200 mL) twice, saturated $NaHCO_3$ solution (200 mL) and water. The organic phase was separated, dried with anhydrous sodium sulfate, and concentrated under reduced pressure to remove the solvent. The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate 10:1) and vacuum dried to afford N^1,N^4-diacetyl–N^1,N^4-bis(2,5-dimethoxybenzyl)fumaramide (7.47 g, 15 mmol). N^1,N^4-diacetyl–N1,N4-bis(2,5-dimethoxybenzyl)fumaramide (2.8 g, 5.63 mmol), acetonitrile (50 mL), PPh_3 (1.495 g, 5.7 mmol) and pyridinium p-toluene sulfonate (0.7288 g, 2.9 mmol) were added to a 100 mL round bottom flask. The reaction mixture was stirred at 100 °C (oil bath) for 10 h. After the reaction, it was cooled to room temperature, and the yellow solid was separated. The reaction mixture was concentrated under reduced pressure to remove the acetonitrile solvent. The residual solid was dissolved in dichloromethane (200 mL) and extracted with water (200 mL). The organic phase was separated, dried with anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 8:1) to produce 2,5-bis(2,5-dimethoxybenzyl)-3,6-dimethyl-2,5-di-

hydropyrrolo[3,4-c]pyrrole-1,4-dione (1.7 g, 3.66 mmol) as a green solid. Crystals of the title compound were obtained by slow vaporization of a solution in CH_2Cl_2 within one week.

2 Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

3 Comment

Diketopyrrolopyrrole (DPP), which was discovered in 1974, has become one of the most widely used prototypical π-cores for organic electronic devices and high performance pigments.[3–6] The conventional synthesis of the DPP core involves heating a mixture of aromatic nitrile (Ar–CN) and succinic acid ester in the presence of a strong base such as potassium tert-butoxide (KOtBu), giving rise to a DPP unit bearing two aromatic rings at the 3,6-positions.[7,8] In 2019, Scott and co-workers reported the efficient synthesis of a new DPP scaffold, 2,5-dibutyl-3,6-dimethyl-1H,2H,4H,5H-pyrrolo [3,4-c]pyrrole-1,4-dione, using tandem cyclization of N1,N4-diacetyl–N1,N4-dibutylfumaramide.[9] Recently, Tan's group reported the synthesis of an N-substituted DPP derivative Ph–DPP by Scott's method and obtained molecule exhibited quite sensitive chromogenic and fluorescent responses toward F′.[10] However, none of the diketopyrrole derivatives reported by Scott and Tan have a single crystal structure. Herein, we reported the synthesis of a new DPP derivative 2,5-bis(2,5-dimethoxybenzyl)-3,6-dimethyl-2,5-dihydropyrrolo [3,4-c]pyrrole-1,4-dione, which may enrich the DPP chemistry. The title compound, built up by the $C_{26}H_{28}N_2O_6$ molecules, has been synthesized. The single-crystal structure verifies that all bond lengths are in normal ranges [11].

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

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

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