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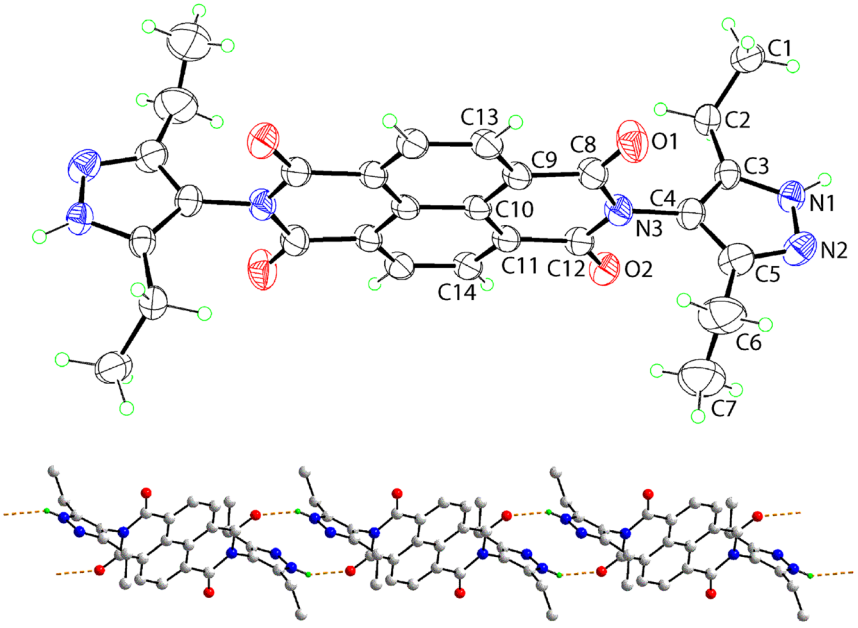
Crystal structure of 2,7-bis(3,5-diethyl-1*H*-pyrazol-4-yl)-benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone, $C_{28}H_{26}N_6O_4$



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Abstract

$C_{28}H_{26}N_6O_4$, trigonal, $R\overline{3}$ (no. 148), a = 20.3056(12) Å, c = 16.3655(10) Å, V = 5843.7(8) Å^3, Z = 9, $R_{gt}(F)$ = 0.0511, $wR_{ref}(F^2)$ = 0.1523, T = 178 K.

CCDC no.: 2481586

Table 1: Data collection and handling.

Crystal:	Orange block
Size	0.20 × 0.15 × 0.09 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω scan
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11,534, 2,649, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,792
$N(param)_{refined}$:	185
Programs:	Rigaku,[1] IL MILIONE,[2] SHELX,[3] WinGX[4]

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data; 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 synthesis of 3,5-diethyl-1-pyrazol-4-amine was accomplished in a three-step process. **LHpzH**: The 3,5-diethyl-1*H*-pyrazole, was obtained by a modified literature method,[5] by

the reaction of 3,5-heptanedione (10.0 g, 78.1 mmol) with hydrazine monohydrate (12.4 mL, 248 mmol, 3.2 equiv.) in ethanol (35 mL) at 373 K for 4 h. After 4 h, the solution was evaporated under vacuum to yield a pale-yellow powder (10.02 g, 80.7 mmol, 103 % yield; the high yield arises due to the presence of some water which was not detectable in the ^{1}H NMR). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.24 (t, 6H, 7.5 Hz, CH_2CH_3), 2.65 (q, 4H, 7.5 Hz, CH_2CH_3), 5.88 (s, 1H, pz-4H); NpzH not observed. **LNO$_2$pzH**: 3,5–Diethyl-1*H*-pyrazol-4-nitro was obtained by a modified literature method.[5] The nitration reaction of LHpzH (5.06 g, 40.7 mmol) was achieved using a mixture of concentrated nitric acid (16 mL) and concentrated sulfuric acid (25 mL). After heating at 373 K for 4 h, the cooled reaction mixture was neutralised with sodium hydroxide solution. After the filtration of the precipitated pale-yellow powder, the obtained powder was carefully washed with distilled water. Crystallization from dichloromethane/heptane (2:1 v/v) solution at 273 K yielded a white powder (4.77 g 28.2 mmol, 69 % yield). Anal. calcd. for $C_7H_{11}N_3O_2{\cdot}1/6(H_2O)$ C 48.83, H 6.63, N 24.40 %. Found: C 49.18, H 6.75, N 24.07 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.31 (t, 6H, 7.5 Hz, CH_2CH_3), 3.03 (q, 4H, 7.5 Hz, CH_2CH_3); NpzH not observed. **LNH$_2$pzH**: 3,5–Diethyl-1*H*-pyrazol-4-amine was obtained by a hydrogenation reaction with palladium on carbon (10 %) catalyst under H_2 (1 atm). After drying, LNO_2pzH (0.83 g, 4.91 mmol) and Pd/C catalyst (1.0 g) were suspended in methanol (30 mL), and the atmosphere was changed from Ar to H_2. The reaction was performed for 4 days at room temperature. The obtained reaction mixture was filtered through Celite to remove undissolved solids. The filtrate was crystallized from dichloromethane at 243 K to yield a colourless powder (0.59 g, 4.24 mmol, 86 % yield). Anal. calcd. for $C_7H_{13}N_3$: C 60.40, H 9.41, N 30.19 %. Found: C 60.05, H 9.68, N 30.13 %. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.25 (t, 6H, 7.5 Hz, CH_2CH_3), 2.59 (q, 4H, 7.5 Hz, CH_2CH_3); NpzH and NH_2 not observed. IR (KBr, cm^{-1}): 3,358 s ν(NH_2), 3,291 s ν(N–H), 3,209 s ν(N–H), 2,972 s ν(C–H), 2,935 s ν(C–H), 2,874 s ν(C–H), 1,602 s ν(C=N). Under an Ar atmosphere, the reaction of 3,5-diethyl-1*H*-pyrazol-4-amine (0.278 g, 2.00 mmol) with naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.236 g, 0.88 mmol) in anhydrous *N*,*N*-dimethylformamide (10 mL) was conducted by solvothermal synthesis for 6 days at 393 K. The solvent was then removed in vacuo to yield a brown powder. The brown powder was recrystallized from an anhydrous methanol solution at 273 K to yield a brown powder (0.354 g, 0.693 mmol, 69 % yield). Single crystals for X-ray crystallography were obtained by the slow evaporation at room temperature from an anhydrous acetone solution. **Anal. calcd.** for $C_{28}H_{26}N_6O_4.0.25(H_2O)$: C 65.29, H 5.19, N 16.32 %. Found: C 65.47, H 5.25, N 16.19 %. **^{1}H NMR** ($CDCl_3$, 500 MHz): 1.21 (t, 12H, 7.5 Hz, CH_2CH_3), 2.53 (q, 8H, 7.5 Hz, CH_2CH_3), 8.87 (s, 4H, Ph–*H*); NpzH not observed. **IR** (KBr, cm^{-1}): 3,613 m, 3,362 s ν(N–H), 3,078 s ν(C–H), 2,974 s ν(C–H), 2,936 s ν(C–H), 2,877 s ν(C–H), 1,712 s ν(C=O), 1,678 s ν(C=O), 1,582 s ν(C=N).

2 Experimental details

The N- and C-bound H atoms were geometrically placed (N–H = 0.88 Å and C–H = 0.95–0.99 Å) and refined as riding with U_{iso} (H) = 1.2–1.5U_{eq} (N, C). The C7-methyl group was disordered over two sites. Each component was refined independently with anisotropic displacement parameters. The major component had a site occupancy factor = 0.768(8). The unit-cell has solvent accessible voids of 104 Å^3; see CIF for further details.

3 Discussion

Recently, we described the synthesis and crystallographic characterization of two 4-amino-pyrazoles,[5,6] of particular interest since the amino group can be subsequently reacted with different carbonyl functional groups such as aldehyde,[7] carboxylic acid[8] and, as demonstrated herein, carboxylic anhydride. This chemistry opens a new field for the exploration of new, high-dimensional materials.[9] In the present study, the synthesis of a new 4-amino-pyrazole is described, viz. 3,5-diethyl-1*H*-pyrazol-4-amine, and the product of its reaction with naphthalene-1,4,5,8-tetracarboxylic dianhydride to give the title compound, (I) {systematic name: 6,13-bis(3,5-diethyl-1*H*-pyrazol-4-yl)-6,13- diazatetracyclo[6.6.2.0$^{\{4,16\}.0}${1,15}]hexadeca-1,3,8,10,15-pentaene-5,7,12,14-tetrone}. Some related chemistry has been published with naphthalene-1,4,5,8-tetracarboxylic dianhydride.[10,11]

After the nitration reaction of **LHpzH** with a mixture of concentrated nitric acid and concentrated sulfuric acid, a new compound **LNO$_2$pzH** was obtained in 69 % yield.[6] The hydrogenation reaction of **LNO$_2$pzH** with palladium on carbon (10 %) catalyst under an H_2 (1 atm) atmosphere yielded a colourless powder of **LNH$_2$pzH** in 86 % yield. This material, **LNH$_2$pzH**, can be also obtained by a modified method using $NaNO_2$/HCl/NH_2NH_2.[6] However, the latter reaction yielded the product in low yield, i.e. 28 %. The IR spectrum of **LNH$_2$pzH** features a characteristic absorption band at 3,358 cm^{-1}, assigned to amine–NH_2 stretching and a

strong absorption band at 3,291 cm^{-1} which is assigned to pyrazolyl–N–H stretching. The expected signals in the ^{1}H NMR spectrum of **LNH$_2$pzH** at 1.25 ppm (methyl–H) and 2.59 ppm (methylene–H), are shifted upfield compared to those of the precursor, **LNO$_2$pzH**, at 1.31 ppm and 3.03 ppm. New, characteristic absorption bands were observed in the IR spectrum of (I). Thus, the sharp N–H$_2$ stretching band in the spectrum of the **LNH$_2$pzH** precursor disappeared and the band at 3,291 cm^{-1} was shifted to 3,362 cm^{-1} in the spectrum of (I). The C=N stretching bands of **LNH$_2$pzH** at 1,602 cm^{-1} was clearly shifted to 1,582 cm^{-1} in (I), and two new C=O bands at 1,712 and 1,678 cm^{-1} were observed and shifted from 1,781 to 1,766 cm^{-1} observed for naphthalene-1,4,5,8-tetracarboxylic dianhydride.

The molecular structure of (I) is illustrated in the upper view of the figure (35 % displacement ellipsoids; the minor part of the disorder is omitted for clarity). The molecule is disposed about a centre of inversion and comprises a central tetrone molecule [r.m.s. = 0.044 Å; maximum deviation = +/−0.090(2) for the C8 atoms] connected at each nitrogen atom to a 3,5-diethyl-1*H*-pyrazol-4-yl ring. The dihedral angle between the N1- and N3-rings is 80.94(11)°, indicating a near to perpendicular relationship. The confirmation of protonation at the N1 atom in the pyrazolyl ring rather than at the N2 atom is seen in the disparity in the C3–N1–N2 [113.84(16)°] and C5–N2–N1 [104.19(17)°] angles and in the pattern of hydrogen-bonding (see below). Within the pyrazolyl ring, the C3–N1 [1.350(2) Å] bond length is significantly longer than the C5–N2 [1.333(3) Å] bond. In the same way, C4–C5 [1.399(3) Å] is longer than the C3–C4 [1.364(3) Å] bond; the N1–N2 bond length is 1.352(2) Å. These results suggest limited delocalisation of π-electron density over the five-membered ring. The ethyl groups on each pyrazolyl residue lies to opposite sides of the ring.

Conventional hydrogen-bonding features in the molecular packing, namely pyrazolyl–N–H···O(carbonyl) [N1–H1n···O2^i: H1n···O2^i = 2.19 Å, N1···O2^i = 2.885(2) Å with the angle subtended at H1n = 136° for symmetry operation (i) 7/3 – x, 2/3 – y, 2/3 – z] interactions which occur within linear chains approximately parallel to [2 0 1], as illustrated in the lower view of the figure (non-acidic hydrogen atoms have been omitted for clarity).

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