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Crystal structure of 8,8'-di-*p*-tolyl-8'*H*-7,8'-biacenaphtho[1,2-*d*]imidazole, C₄₀H₂₆N₄

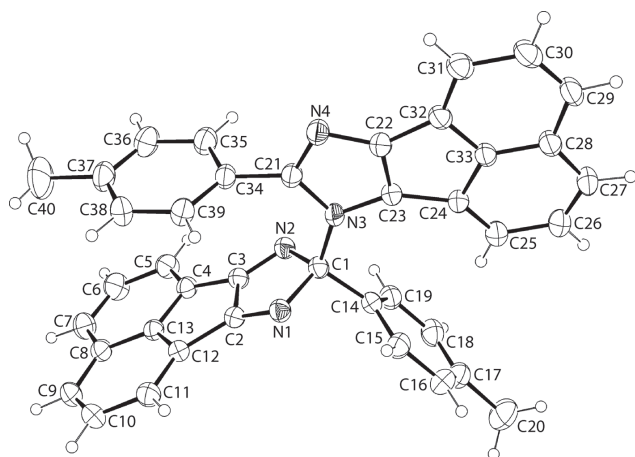


Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.42 × 0.36 × 0.19 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
θ_{\max} , completeness:	29.4°, >85% (up to 25.2°, >99%)
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11508, 6653, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 4449
$N(\text{param})_{\text{refined}}$:	399
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], ORTEP [4], PLATON [5]

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Abstract

C₄₀H₂₆N₄, triclinic, $P\bar{1}$ (no. 2), $a = 9.5201(6)$ Å, $b = 12.1701(8)$ Å, $c = 12.8721(7)$ Å, $\alpha = 79.949(5)^\circ$, $\beta = 88.350(5)^\circ$, $\gamma = 75.893(6)^\circ$, $V = 1424.05(16)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0519$, $wR_{\text{ref}}(F^2) = 0.1403$, $T = 293$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Source of material

In the dark, a freshly prepared solution of potassium ferri-cyanide (2.12 g, 6.44 mmol) and potassium hydroxide (1.08 g, 19.33 mmol) in water (200 mL) was added over a period of 0.5 h to 8-(*p*-tolyl)-7*H*-acenaphtho [1,2-*d*]imidazole ([6], 1 g, 3.54 mmol) in benzene (100 mL) in an ice-bath with vigorous stirring. The reaction mixture was stirred overnight at room temperature. The organic layer was collected and washed three times with water, and the aqueous phase was extracted with benzene three times and combined. The solution was dried over sodium sulfate, evaporated and dried. The radical dimerization reaction gave the title compound. The resulting solid was recrystallised from benzene/ethanol to give orange crystals. Yield: 67%. M.p. (Stuart Scientific Co. Ltd apparatus): 519–521 K. IR (PerkinElmer spectrum 100 FT-IR spectrophotometer; $\nu(\text{max})$, cm⁻¹): 3072, 3023 (aromatic-CH stretch), 2969, 2860 (CH₃ stretch), 1429, 1369 (CH₃ bend), 1638 (C=N), 1608, 1484 (C=C), 1281 (C–N).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.96 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2–1.5U_{\text{eq}}(\text{C})$.

Discussion

Imidazole- and π -expanded imidazole derivatives are emission-tuneable, fluorescent dyes and have been reported to display excited-state intramolecular proton transfer (ESIPT) properties [7]. In this context, molecules directly

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
N1	0.09336(15)	0.60751(12)	0.08070(11)	0.0375(3)
N2	0.17612(16)	0.78196(12)	0.08356(11)	0.0376(3)
N3	-0.07447(15)	0.78009(13)	0.11978(10)	0.0374(3)
N4	-0.28285(17)	0.87236(14)	0.03069(11)	0.0430(4)
C1	0.07569(18)	0.71149(15)	0.13328(13)	0.0363(4)
C2	0.20016(18)	0.61409(15)	0.01937(13)	0.0351(4)
C3	0.24928(18)	0.72045(15)	0.02039(13)	0.0351(4)
C4	0.36740(19)	0.72264(15)	-0.05458(13)	0.0372(4)
C5	0.4534(2)	0.79618(17)	-0.08922(15)	0.0475(5)
H5	0.4426	0.8646	-0.0636	0.057*
C6	0.5589(2)	0.7653(2)	-0.16484(17)	0.0580(6)
H6	0.6185	0.8145	-0.1884	0.070*
C7	0.5771(2)	0.66628(19)	-0.20490(16)	0.0546(5)
H7	0.6481	0.6496	-0.2548	0.066*
C8	0.4892(2)	0.58832(17)	-0.17133(14)	0.0422(4)
C9	0.4955(2)	0.48285(18)	-0.20522(15)	0.0509(5)
H9	0.5635	0.4583	-0.2549	0.061*
C10	0.4026(2)	0.41671(18)	-0.16574(15)	0.0529(5)
H10	0.4093	0.3477	-0.1894	0.063*
C11	0.2974(2)	0.44906(16)	-0.09058(14)	0.0463(5)
H11	0.2348	0.4028	-0.0655	0.056*
C12	0.28900(19)	0.54982(15)	-0.05528(13)	0.0364(4)
C13	0.38521(18)	0.61925(15)	-0.09622(13)	0.0356(4)
C14	0.12037(19)	0.66553(15)	0.24796(13)	0.0380(4)
C15	0.0851(2)	0.56613(17)	0.29962(14)	0.0475(5)
H15	0.0256	0.5322	0.2663	0.057*
C16	0.1378(3)	0.51719(19)	0.40020(16)	0.0576(6)
H16	0.1126	0.4508	0.4339	0.069*
C17	0.2275(2)	0.5651(2)	0.45208(15)	0.0559(5)
C18	0.2597(2)	0.66566(19)	0.40050(15)	0.0527(5)
H18	0.3180	0.7003	0.4341	0.063*
C19	0.2067(2)	0.71534(17)	0.29999(14)	0.0450(4)
H19	0.2294	0.7830	0.2670	0.054*
C20	0.2881(3)	0.5089(3)	0.56069(18)	0.0851(8)
H20A	0.3592	0.5463	0.5796	0.128*
H20B	0.3325	0.4291	0.5608	0.128*
H20C	0.2112	0.5155	0.6109	0.128*
C21	-0.14360(19)	0.82479(16)	0.02182(13)	0.0389(4)
C22	-0.30516(19)	0.85873(15)	0.13727(13)	0.0391(4)
C23	-0.18093(19)	0.80445(15)	0.19418(13)	0.0370(4)
C24	-0.2097(2)	0.80177(15)	0.30815(13)	0.0393(4)
C25	-0.1361(2)	0.77285(18)	0.40235(14)	0.0518(5)
H25	-0.0365	0.7421	0.4047	0.062*
C26	-0.2124(3)	0.7901(2)	0.49593(16)	0.0597(6)
H26	-0.1607	0.7706	0.5594	0.072*
C27	-0.3586(3)	0.83407(19)	0.49774(16)	0.0573(6)
H27	-0.4051	0.8412	0.5616	0.069*
C28	-0.4388(2)	0.86878(16)	0.40162(15)	0.0462(5)
C29	-0.5883(2)	0.92308(18)	0.38879(17)	0.0533(5)
H29	-0.6447	0.9351	0.4478	0.064*
C30	-0.6500(2)	0.95787(18)	0.29062(17)	0.0545(5)
H30	-0.7484	0.9934	0.2844	0.065*
C31	-0.5700(2)	0.94192(17)	0.19772(16)	0.0485(5)
H31	-0.6145	0.9664	0.1315	0.058*
C32	-0.42543(19)	0.88945(15)	0.20800(14)	0.0400(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C33	-0.3615(2)	0.85235(15)	0.31000(14)	0.0390(4)
C34	-0.06952(19)	0.82818(16)	-0.08100(13)	0.0400(4)
C35	-0.0198(2)	0.92410(18)	-0.12243(15)	0.0525(5)
H35	-0.0348	0.9855	-0.0860	0.063*
C36	0.0519(3)	0.9298(2)	-0.21698(16)	0.0604(6)
H36	0.0855	0.9949	-0.2430	0.072*
C37	0.0748(2)	0.8414(2)	-0.27379(16)	0.0586(6)
C38	0.0204(2)	0.7473(2)	-0.23408(15)	0.0577(6)
H38	0.0320	0.6876	-0.2723	0.069*
C39	-0.0506(2)	0.73986(18)	-0.13918(14)	0.0487(5)
H39	-0.0860	0.6755	-0.1141	0.058*
C40	0.1586(4)	0.8472(3)	-0.3754(2)	0.1058(11)
H40A	0.1132	0.9153	-0.4236	0.159*
H40B	0.1597	0.7806	-0.4063	0.159*
H40C	0.2562	0.8492	-0.3608	0.159*

related to the title compound are readily prepared from the cyclocondensation of 4',7'-phenanthroline-5',6'-dione with various aldehydes followed by oxidative dimerization in the presence of hexacyanoferrate [8]. In the absence of structural data for these dimeric species, herein, the crystal and molecular structures of the title compound are described, adding to a complementary structure report [9].

The molecular structure of the title compound comprises 2,2-disubstituted imidazole (N1-ring) and N-substituted imidazole (N3-ring) rings connected by a N3–C1 bond [1.467(2) Å]. The different substitution patterns in the imidazole rings results in very different bond lengths within the five-membered cycles. The presence of formal C=N bonds in the N1-ring is seen in the N1–C2 and N2–C3 bond lengths of 1.279(2) and 1.278(2) Å, respectively, which are shorter than the equivalent bond lengths for the N3-ring of 1.389(2) Å [N3–C23] and 1.370(2) Å [N4–C22]. Consistent with this observation are the systematic variations in the remaining two C–N bonds in each ring. These have elongated considerably in the N1-ring with N1–C1 = 1.509(2) Å and N2–C1 = 1.494(2) Å compared to the N2–C2 and N3–C2 bonds. However, for the N3-ring, bonds have either elongated [N3–C21 = 1.397(2) Å] or shortened [N4–C21 = 1.321(2) Å] reflecting some double-bond character in the N4–C21 bond. Finally, the C–C bond lengths in the N1-ring [C2–C3 = 1.482(2) Å] and N3-ring [C22–C23 = 1.368(2) Å] follow the expected trends. Each of the five-membered rings is planar. The N1-ring has a r.m.s. deviation of 0.041 Å for the five atoms with the maximum deviation from the least-squares plane being 0.034(2) Å for the C1 atom. The N3-ring is considerably more planar, exhibiting a r.m.s. deviation of 0.008 Å and a maximum deviation of 0.007(2) Å for the N3 atom. As might be

expected, the delocalization of π -electron density extends over the entire residue and consistent with this, is the r.m.s. deviation of 0.018 Å for the 15 atoms, N1, N2, C1–C13; for the N3, N4, C21–C33 atoms, the r.m.s. deviation is 0.048 Å. The dihedral angle between the two 15-membered residues is 83.07(3)°, indicating an almost orthogonal relationship. Finally, the dihedral angle between the 15-membered residue with the N3 atom and appended C34-tolyl residue is 89.47(5)°, also indicating an orthogonal relationship.

In the molecular packing, extensive π – π and C–H $\cdots\pi$ interactions are evident and cooperate to sustain the three-dimensional architecture. The most prominent π – π interaction occurs between (C2–C4, C12, C13) and (C8–C13) rings [inter-centroid distance = 3.6163(11) Å, angle of inclination = 0.23(9)° for symmetry operation: 1-x, 1-y, -z]. The shortest and most directional C–H $\cdots\pi$ interaction is a phenyl-C9–H $\cdots\pi$ (C14–C19) contact [H9 \cdots ring centroid separation = 2.78 Å, C9 \cdots ring centroid = 3.672(2) Å, angle at H9 = 161° for symmetry operation: 1-x, 1-y, -z].

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