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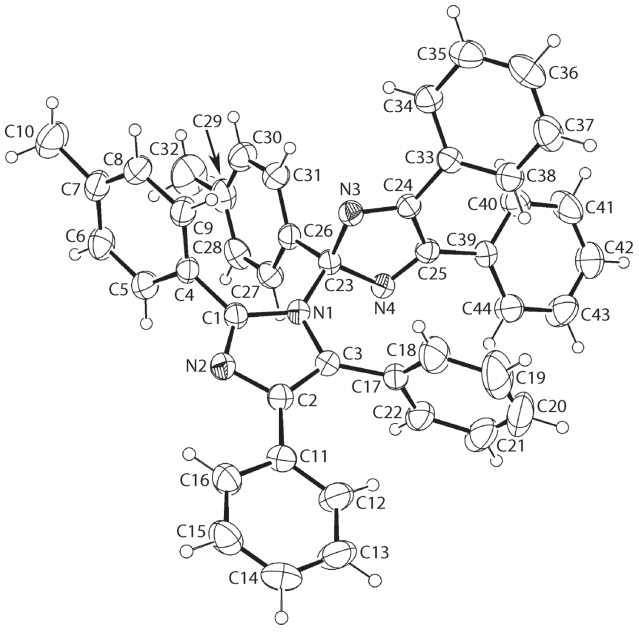
Crystal structure of 4,4′,5,5′-tetraphenyl-2,2′-di-*p*-tolyl-2′*H*-1,2′-biimidazole, $C_{44}H_{34}N_4$



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Abstract

$C_{44}H_{34}N_4$, monoclinic, $P2_1$ (no. 4), $a = 10.1233(5)$ Å, $b = 12.1414(7)$ Å, $c = 13.7420(7)$ Å, $\beta = 98.389(5)°$, $V = 1670.97(15)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0452$, $wR_{ref}(F^2) = 0.1136$, $T = 293(2)$ K.

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

Table 1: Data collection and handling.

Crystal:	Block, pale-yellow
Size:	0.34 × 0.17 × 0.14 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.07 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω-scans
θ_{max}, completeness:	29.1°, >93% (up to 25.2°, >99%)
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	29323, 7950, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5874
$N(param)_{refined}$:	435
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], ORTEP [4], PLATON [5]

Source of material

In the dark, a freshly prepared solution of potassium ferricyanide (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 4,5-diphenyl-2-(*p*-tolyl)-1*H*-imidazole ([6]; 0.50 g, 1.61 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, the water phase was extracted with benzene three times and the extracts combined. The solution was dried over sodium sulfate, evaporated and dried. The radical dimerization reaction of 4,5-diphenyl-2-(*p*-tolyl) imidazole leads to the title compound. The resulting solid was recrystallized from benzene/ethanol to yield pale-yellow crystals. Yield: 88%. M.p. (Stuart Scientific Co. Ltd apparatus): 447−478 K. **IR** (PerkinElmer spectrum 100 FT-IR spectrophotometer; ν(max), cm^{-1}): 3052, 3028 (aromatic-CH stretch), 1602, 1489 (C=C), 2917, 2860 (CH_3 stretch), 1443, 1378 (CH_3 bend).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.93−0.96 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. Owing to poor agreement, one reflection, i.e. (0 12 4), was omitted from the final cycles of refinement. The absolute structure was not determined.

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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}
N1	0.7808(2)	0.50587(18)	0.38400(14)	0.0434(5)
N2	0.7473(2)	0.35019(19)	0.46181(15)	0.0497(5)
N3	0.9634(2)	0.62458(17)	0.36063(15)	0.0444(5)
N4	0.7464(2)	0.66410(18)	0.27409(14)	0.0445(5)
C1	0.7823(3)	0.4536(2)	0.47324(18)	0.0458(6)
C2	0.7240(3)	0.3314(2)	0.36105(19)	0.0482(6)
C3	0.7457(3)	0.4261(2)	0.31187(18)	0.0449(6)
C4	0.8217(3)	0.5038(2)	0.57186(18)	0.0458(6)
C5	0.7271(3)	0.5236(3)	0.6322(2)	0.0609(8)
H5	0.6383	0.5053	0.6111	0.073*
C6	0.7631(3)	0.5707(3)	0.7241(2)	0.0656(8)
H6	0.6977	0.5850	0.7634	0.079*
C7	0.8936(3)	0.5966(3)	0.7580(2)	0.0606(8)
C8	0.9881(3)	0.5727(3)	0.6988(2)	0.0647(8)
H8	1.0774	0.5877	0.7212	0.078*
C9	0.9532(3)	0.5270(3)	0.60663(19)	0.0575(7)
H9	1.0190	0.5117	0.5678	0.069*
C10	0.9313(5)	0.6534(4)	0.8560(2)	0.0917(12)
H10A	0.8981	0.6116	0.9066	0.138*
H10B	0.8931	0.7259	0.8531	0.138*
H10C	1.0268	0.6588	0.8706	0.138*
C11	0.6861(3)	0.2188(2)	0.3248(2)	0.0511(6)
C12	0.6465(4)	0.1945(3)	0.2266(2)	0.0734(10)
H12	0.6400	0.2511	0.1805	0.088*
C13	0.6164(4)	0.0883(3)	0.1956(3)	0.0850(11)
H13	0.5908	0.0743	0.1290	0.102*
C14	0.6237(3)	0.0027(3)	0.2618(3)	0.0745(9)
H14	0.6027	−0.0688	0.2408	0.089*
C15	0.6624(4)	0.0255(3)	0.3590(3)	0.0742(9)
H15	0.6681	−0.0312	0.4049	0.089*
C16	0.6932(3)	0.1318(3)	0.3899(2)	0.0650(8)
H16	0.7194	0.1451	0.4565	0.078*
C17	0.7402(3)	0.4411(2)	0.20454(19)	0.0527(7)
C18	0.8513(4)	0.4190(3)	0.1614(3)	0.0826(11)
H18	0.9327	0.4042	0.2000	0.099*
C19	0.8409(8)	0.4190(5)	0.0605(4)	0.126(2)
H19	0.9164	0.4038	0.0316	0.152*
C20	0.7253(10)	0.4404(4)	0.0025(3)	0.133(3)
H20	0.7209	0.4393	−0.0656	0.159*
C21	0.6136(7)	0.4639(4)	0.0446(3)	0.1093(18)
H21	0.5331	0.4792	0.0050	0.131*
C22	0.6207(4)	0.4650(3)	0.1457(2)	0.0720(10)
H22	0.5453	0.4817	0.1742	0.086*
C23	0.8199(3)	0.6209(2)	0.36718(17)	0.0423(6)
C24	0.9733(2)	0.6730(2)	0.27926(17)	0.0421(5)
C25	0.8366(3)	0.7017(2)	0.22627(17)	0.0430(5)
C26	0.7823(3)	0.6999(2)	0.44552(17)	0.0454(6)
C27	0.6487(3)	0.7102(2)	0.4565(2)	0.0527(6)
H27	0.5847	0.6678	0.4180	0.063*
C28	0.6102(3)	0.7831(3)	0.5243(2)	0.0637(8)
H28	0.5204	0.7883	0.5313	0.076*
C29	0.7021(4)	0.8482(3)	0.5817(2)	0.0679(9)
C30	0.8348(4)	0.8392(3)	0.5689(2)	0.0675(9)
H30	0.8982	0.8830	0.6065	0.081*
C31	0.8754(3)	0.7661(3)	0.5010(2)	0.0576(7)
H31	0.9650	0.7619	0.4931	0.069*
C32	0.6581(6)	0.9274(4)	0.6556(3)	0.1152(17)
H32A	0.6105	0.8878	0.7001	0.173*
H32B	0.6007	0.9824	0.6217	0.173*
H32C	0.7350	0.9622	0.6920	0.173*
C33	1.1028(2)	0.6926(2)	0.24390(18)	0.0445(6)
C34	1.2098(3)	0.7323(2)	0.3082(2)	0.0543(7)
H34	1.1999	0.7489	0.3728	0.065*
C35	1.3323(3)	0.7474(3)	0.2760(3)	0.0706(9)
H35	1.4042	0.7753	0.3187	0.085*
C36	1.3473(3)	0.7211(3)	0.1812(3)	0.0764(10)
H36	1.4300	0.7295	0.1604	0.092*
C37	1.2411(4)	0.6824(3)	0.1169(2)	0.0731(9)
H37	1.2517	0.6653	0.0525	0.088*
C38	1.1188(3)	0.6689(3)	0.1478(2)	0.0590(7)
H38	1.0465	0.6436	0.1038	0.071*
C39	0.8039(3)	0.7665(2)	0.13505(18)	0.0454(6)
C40	0.8770(3)	0.8589(3)	0.1182(2)	0.0677(9)
H40	0.9506	0.8794	0.1633	0.081*
C41	0.8405(4)	0.9208(3)	0.0341(3)	0.0836(11)
H41	0.8880	0.9844	0.0243	0.100*
C42	0.7370(4)	0.8903(3)	−0.0339(3)	0.0823(11)
H42	0.7145	0.9317	−0.0908	0.099*
C43	0.6659(4)	0.7983(3)	−0.0185(2)	0.0811(11)
H43	0.5959	0.7760	−0.0658	0.097*
C44	0.6972(3)	0.7381(3)	0.0668(2)	0.0630(8)
H44	0.6452	0.6776	0.0781	0.076*

Discussion

An accompanying paper [7] describes the first example of a structure related to that of the title compound, featuring two distinct imidazole residues linked by a C—N bond. Interest in these materials relates to the potentially useful characteristics exhibited by imidazole- and π-expanded imidazole derivatives in that these fluorescent dyes are emission-tuneable [8]. Herein, the crystal and molecular structures of the title compound are described, and compared with the literature precedent, namely 8,8′-di-*p*-tolyl-8′*H*-7,8′-biacenaphtho[1,2-*d*]imidazole [7].

The molecular structure of the title compound displays two distinct imidazole residues connected by a N1—C23 bond [1.479(3) Å]. The N1-imidazole ring is planar and exhibits a r.m.s. deviation for the fitted atoms of 0.012 Å. Based on the N2—C1 bond [1.308(4) Å] being significantly shorter than either of the N1—C1 [1.379(3) Å], N1—C3 [1.394(3) Å] and N2—C2 [1.389(3) Å] bonds, and that the C2—C3 bond is relatively short [1.368(4) Å], it is concluded the N2—C1 and C2—C3 bonds correspond to double bonds. A different situation pertains in the N3-imidazole ring. While the r.m.s. deviation for planarity is 0.048 Å, there are significant deviations from the

least-squares plane, e.g. 0.043(2) Å for the N4 atom. Therefore, the ring is best described as being twisted about the N4—C23 bond. The short N3—C24 [1.280(3) Å] and N4—C25 [1.284(3) Å] bonds compared with N3—C23 [1.469(3) Å] and N4—C23 [1.479(3) Å] bonds indicate the former are to be considered as double bonds. Consistent with this observation, the C24—C25 bond length of 1.508(3) Å corresponds to a single bond. While these results largely match those reported for 8,8′-di-*p*-tolyl-8′*H*-7,8′-biacenaphtho[1,2-*d*]imidazole [7], the corresponding ring did not exhibit a significant twist.

In terms of conformation, the dihedral angle between the two imidazole rings is 75.45(15)° indicating an almost orthogonal relationship, mirroring the same observation noted for 8,8′-di-p-tolyl-8′H-7,8′-biacenaphtho[1,2-d]imidazole [7]. The dihedral angles between the N1-ring and the C1-, C2-, and C3-appended rings are 72.36(16), 9.40(17) and 89.15(19)°, respectively, with the significant twists clearly related to the steric pressure exerted by the proximity of the substituted N3-imidazole ring. The dihedral angles between the N3-ring and the C23-, C24-, and C25-appended rings are 71.47(14), 44.01(15) and 42.57(15)°, respectively.

As a general observation, 4,4′,5,5′-tetraphenyl-2,2′-di-p-tolyl-2′H-1,2′-biimidazole is less sterically encumbered compared to 8,8′-di-p-tolyl-8′H-7,8′-biacenaphtho[1,2-d]imidazole [7]. This is seen by the partipation of the imidazole-N2 atom in an intermolecular interaction whereas no such contact was noted in the analogous compound [7]. Thus, phenyl-C34—H34$\cdots$N2(imidazole) contacts [H34$\cdots$N2^{i} = 2.57 Å, C34$\cdots$N2^{i} = 3.439(3) Å and angle at H34 = 156° for i: $2-x$, $1/2+y$, $1-z$] lead to supramolecular chains with a helical topology (2_1 screw symmetry) along the *b*-axis. The links within chains are reinforced by phenyl-C—H$\cdots\pi$(tolyl) and tolyl-C—H$\cdots\pi$(phenyl) interactions. The chains pack in the crystal without directional interactions between them.

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