Crystal structure of (2,6-diisopropyl-phenyl)-[6-(2,6-dimethyl-phenyl)-pyridin-2-yl-methylene]-amine, $C_{26}H_{30}N_2$

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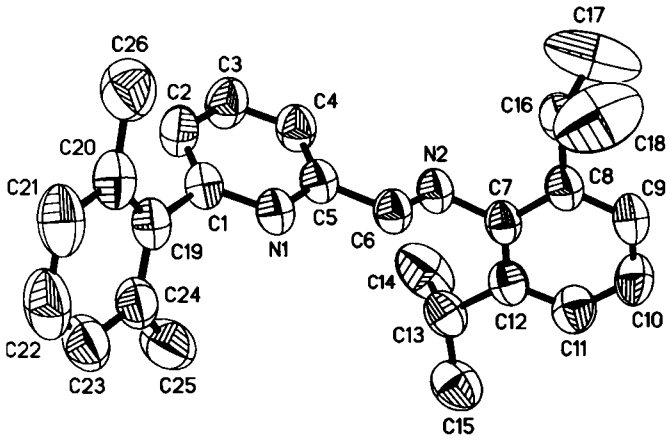

Abstract

$C_{26}H_{30}N_2$, monoclinic, *C*12/*c*1 (no. 15), a = 20.434(2) Å, b = 8.551(1) Å, c = 26.498(2) Å, β = 102.889(1)°, V = 4513.4 Å^3, Z = 8, $R_{gt}(F)$ = 0.062, $wR_{ref}(F^2)$ = 0.187, T = 293 K.

Source of material

First, 2.0 g (10.7 mmol) of 6-bromopyridine-2-carbaldehyde and 2.03 mL (1.91 g, 10.7 mmol) of 2,6-diisopropylaniline were dissolved in 30 mL of ethanol and the mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure and 3.59 g (97 %) of pale yellow crystalline material (**I**) was obtained and used without further purification. A solution of 1.39 mL (1.93 g, 10.4 mmol) of 2-bromo-*m*-xylene in 30 mL THF was added to 0.30 g (12.5 mmol) magnesium turnings and the resulting suspension stirred and activated using 0.2 mL of 1,2-bromoethane. An exothermic reaction took place and an ice bath was used to cool the reaction mixture when the reaction became too vigorous. The reaction mixture was stirred at room temperature for 2 h, then filtered and the filtrate (**II**) directly used.

To a solution of 3.0 g (8.69 mmol) **I** in 30 mL of dioxane was added a suspension of 0.11 g (0.87 mmol) $FeCl_2$ in 10 mL of THF. The Grignard solution **II** was then slowly added to the stirred suspension. The reaction mixture was heated to 70 °C for 48 h. 100 mL of water and 80 mL of diethyl ether were added and the resulting suspension transferred to a 500 mL separating funnel. The organic phase was collected and the inorganic phase washed with diethyl ether two times and extracted. The combined organic phases were washed with a saturated sodium chloride solution and dried with Na_2SO_4. The organic phase was concentrated to dryness under vacuum resulting in a brown oily product. The oil was purified using silica chromatography (pentane) and then crystallized from pentane at –25 °C to afford pale yellow crystals suitable for X-ray crystal structure analysis (yield 1.16 g (39 %), m.p. 142.5 °C).

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Discussion

As neutral metal complexes are required for selective oligomerization of ethylene or bis-alkoxycarbonylation of styrene, Bianchini and co-workers developed a series of substituted iminopyridine ligands [1-3]. The title compound, our search by SciFinder proceeded without any results, is a new sterically demanding member of this type of ligands. The bulky phenyl substituents in the 6-position of the pyridine and at the imino N atom are twisted with regard to the pyridine ring, and the dihedral angles are 118.6° and 98.1°, respectively. Both phenyl rings form a dihedral angle of 68.8°. The significant shortening of the C6—N2 bond (1.25 Å) indicates the imino function. In the uncoordinated ligand, the free electron pairs at the $N_{pyridine}$ and N_{imino} atoms are *transoid*. The C6–N2–C7 angle with 119.8° is much smaller than the C5–C6–N2 angle with 123.0°.

Table 1. Data collection and handling.

Crystal:	pale yellow prism, size 0.4 × 0.5 × 0.6 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.63 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	52.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	31342, 4468
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3001
$N(param)_{refined}$:	253
Programs:	SIR97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	8*f*	–0.0275	–0.3555	0.3104	0.088
H(3)	8*f*	–0.0779	–0.2539	0.3733	0.098
H(4)	8*f*	–0.0126	–0.1203	0.4430	0.085
H(6)	8*f*	0.1650	–0.0608	0.4627	0.074
H(9)	8*f*	0.2317	0.0372	0.6549	0.092
H(10)	8*f*	0.2624	0.2883	0.6421	0.102
H(11)	8*f*	0.2184	0.4149	0.5656	0.096
H(13)	8*f*	0.1314	0.2503	0.4509	0.093
H(14A)	8*f*	0.0399	0.4166	0.4461	0.203
H(14B)	8*f*	0.0564	0.4292	0.5066	0.203
H(14C)	8*f*	0.0339	0.2686	0.4797	0.203
H(15A)	8*f*	0.2161	0.4401	0.4711	0.154
H(15B)	8*f*	0.1690	0.5446	0.4963	0.154
H(15C)	8*f*	0.1505	0.5113	0.4366	0.154
H(16)	8*f*	0.1242	–0.2013	0.5611	0.102
H(17A)	8*f*	0.0986	–0.2793	0.6390	0.286

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(17B)	8f	0.0690	–0.1127	0.6231	0.286
H(17C)	8f	0.1347	–0.1303	0.6665	0.286
H(18A)	8f	0.1956	–0.3694	0.6141	0.248
H(18B)	8f	0.2386	–0.2277	0.6406	0.248
H(18C)	8f	0.2353	–0.2657	0.5822	0.248
H(21)	8f	0.1406	–0.6676	0.2528	0.111
H(22)	8f	0.1955	–0.4972	0.2102	0.119
H(23)	8f	0.1923	–0.2346	0.2251	0.111
H(25A)	8f	0.1564	–0.0189	0.2623	0.158
H(25B)	8f	0.1492	–0.0420	0.3195	0.158
H(25C)	8f	0.0851	–0.0368	0.2742	0.158
H(26A)	8f	0.0764	–0.7289	0.3106	0.153
H(26B)	8f	0.0223	–0.6039	0.3161	0.153
H(26C)	8f	0.0881	–0.6202	0.3594	0.153

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	8f	0.10467(7)	–0.2075(2)	0.38399(5)	0.0636(8)	0.0667(8)	0.0489(7)	0.0062(6)	0.0107(6)	–0.0049(6)
N(2)	8f	0.09899(7)	0.0007(2)	0.49819(5)	0.0642(8)	0.0771(9)	0.0474(7)	0.0060(6)	0.0104(6)	–0.0061(6)
C(1)	8f	0.06643(8)	–0.2848(2)	0.34385(6)	0.066(1)	0.0654(9)	0.0471(8)	0.0061(7)	0.0077(7)	–0.0028(7)
C(2)	8f	–0.00196(9)	–0.3027(2)	0.33877(7)	0.068(1)	0.090(1)	0.0576(9)	0.0004(9)	0.0051(8)	–0.0144(8)
C(3)	8f	–0.03201(9)	–0.2418(3)	0.37603(8)	0.057(1)	0.113(2)	0.074(1)	–0.003(1)	0.0123(9)	–0.020(1)
C(4)	8f	0.00655(9)	–0.1628(2)	0.41735(7)	0.066(1)	0.089(1)	0.0592(9)	0.0043(9)	0.0176(8)	–0.0111(8)
C(5)	8f	0.07458(8)	–0.1482(2)	0.41973(6)	0.0612(9)	0.0661(9)	0.0483(8)	0.0074(7)	0.0119(7)	–0.0026(6)
C(6)	8f	0.11937(8)	–0.0649(2)	0.46237(6)	0.0599(8)	0.073(1)	0.0522(8)	0.0058(7)	0.0119(7)	–0.0058(7)
C(7)	8f	0.14525(8)	0.0815(2)	0.53769(6)	0.0615(9)	0.071(1)	0.0456(7)	0.0085(7)	0.0127(6)	–0.0068(7)
C(8)	8f	0.17024(9)	0.0047(2)	0.58476(6)	0.072(1)	0.077(1)	0.0499(9)	0.0032(8)	0.0121(7)	–0.0039(7)
C(9)	8f	0.2143(1)	0.0860(2)	0.62343(7)	0.085(1)	0.089(1)	0.0497(9)	0.005(1)	0.0039(8)	–0.0063(8)
C(10)	8f	0.2323(1)	0.2364(3)	0.61593(8)	0.095(1)	0.088(1)	0.064(1)	–0.004(1)	0.003(1)	–0.019(1)
C(11)	8f	0.2062(1)	0.3117(2)	0.56985(8)	0.095(1)	0.068(1)	0.077(1)	0.0022(9)	0.016(1)	–0.0126(9)
C(12)	8f	0.16215(9)	0.2375(2)	0.52964(6)	0.072(1)	0.069(1)	0.0586(9)	0.0128(8)	0.0170(8)	–0.0055(7)
C(13)	8f	0.1311(1)	0.3230(2)	0.47946(7)	0.087(1)	0.079(1)	0.068(1)	0.019(1)	0.0200(9)	0.0080(8)
C(14)	8f	0.0587(2)	0.3630(4)	0.4778(1)	0.106(2)	0.185(3)	0.121(2)	0.065(2)	0.039(2)	0.062(2)
C(15)	8f	0.1703(2)	0.4682(3)	0.4700(1)	0.135(2)	0.079(1)	0.098(2)	0.011(1)	0.031(1)	0.014(1)
C(16)	8f	0.1516(1)	–0.1615(2)	0.59370(8)	0.103(2)	0.086(1)	0.060(1)	–0.011(1)	0.0033(9)	0.0074(9)
C(17)	8f	0.1096(3)	–0.1719(4)	0.6343(2)	0.223(4)	0.124(3)	0.274(5)	0.034(3)	0.161(4)	0.081(3)
C(18)	8f	0.2104(2)	–0.2651(3)	0.6090(2)	0.137(3)	0.076(2)	0.285(5)	0.021(2)	0.052(3)	–0.019(2)
C(19)	8f	0.10237(9)	–0.3473(2)	0.30480(6)	0.0661(9)	0.077(1)	0.0482(8)	0.0069(8)	0.0067(7)	–0.0091(7)
C(20)	8f	0.1038(1)	–0.5078(2)	0.29536(7)	0.084(1)	0.077(1)	0.0576(9)	0.0106(9)	0.0062(8)	–0.0125(8)
C(21)	8f	0.1392(1)	–0.5610(3)	0.25945(8)	0.102(2)	0.102(2)	0.069(1)	0.028(1)	0.010(1)	–0.025(1)
C(22)	8f	0.1718(1)	–0.4594(4)	0.23386(9)	0.092(2)	0.138(2)	0.069(1)	0.019(1)	0.021(1)	–0.033(1)
C(23)	8f	0.1699(1)	–0.3026(3)	0.24282(8)	0.084(1)	0.136(2)	0.062(1)	–0.006(1)	0.023(1)	–0.012(1)
C(24)	8f	0.1350(1)	–0.2426(2)	0.27782(7)	0.077(1)	0.092(1)	0.0546(9)	–0.0018(9)	0.0141(8)	–0.0094(8)
C(25)	8f	0.1311(2)	–0.0697(3)	0.2840(1)	0.151(2)	0.084(2)	0.092(2)	–0.016(1)	0.052(2)	–0.002(1)
C(26)	8f	0.0695(2)	–0.6259(3)	0.3229(1)	0.140(2)	0.076(1)	0.088(1)	0.002(1)	0.023(1)	–0.009(1)

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