Mao-Yuan Zhang and Da-Bin Shi*

Crystal structure of methyl 4′-amino-3′,5′-diisopropyl-[1,1′-biphenyl]-4-carboxylate, $C_{20}H_{25}NO_2$

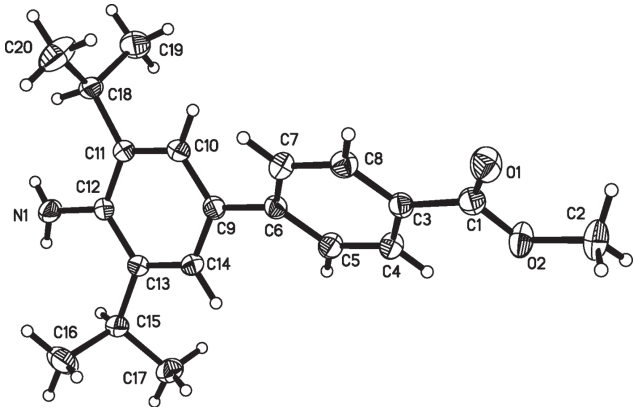

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.8 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	55.4°, 97.6%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10128, 4022, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2790
$N(param)_{refined}$:	221
Programs:	Bruker programs [1], SHELX [2, 3]

https://doi.org/10.1515/ncrs-2017-0324
Received October 20, 2017; accepted February 14, 2018; available online March 3, 2018

Abstract

$C_{20}H_{25}NO_2$, monoclinic, $P2_1/n$ (no. 14), $a = 16.873(4)$ Å, $b = 6.2095(16)$ Å, $c = 16.992(4)$ Å, $\beta = 100.775(4)°$, $V = 1748.9(8)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0473$, $wR_{ref}(F^2) = 0.1417$, $T = 296(2)$ K.

CCDC no.: 1580799

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

Source of materials

Synthesis of 4-iodo-2,6-diisopropylaniline [4, 5]. In a round bottom flask 2,6-di-*iso*-propylaniline (20 mL, 106 mmol, 1.0 equiv) and sodium bicarbonate (26.8 g, 219 mmol, 3.0 equiv) were introduced in MeOH (400 mL). Iodine (29.6 g, 116.5 mmol, 1.1 equiv) in CH_2Cl_2 (200 mL) was added and the mixture was stirred at room temperature for 12 h. Then, solids were filtered off and rinsed with CH_2Cl_2. The filtrate was concentrated under vacuum leading to a dark orange oil. A saturated solution of sodium thiosulfate was added to this oil and stirred for 2 h. After an extraction with CH_2Cl_2, the combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The pure product was obtained as brown oil (23.5 g, 73% yield).

Synthesis of the title compound [6]. A mixture of (4-(methoxycarbonyl)phenyl)boronic acid (15.1 g, 84.17 mmol, 1.1 equiv), 4-iodo-2,6-diisopropylaniline (23.2 g, 76.52 mmol, 1.0 equiv), palladium tetrakis(triphenylphosphine) (1.77 g, 1.53 mmol, 2 mol%), and potassium carbonate (34.8 g, 253 mmol, 3.3 equiv) in 360 mL of dioxane/H_2O (3/1) was stirred under nitrogen for 72 h at 90 °C. After the mixture was cooled to room temperature, it was extracted with CH_2Cl_2 and washed with H_2O. The organic layer was dried with $MgSO_4$, and the solvent was removed. The resulting crude product was purified by column chromatography using silica gel and petroleum ether/ethyl acetate (20/1) as the eluent. The product was obtained (18.08 g, 58.0% yield). Cystals were obtained by slow evaporation of an ethanol solution at room temperature over a period of seven days, yield: 0.58 g (92.5%). **M.p.**: 103–104 °C. **Elemental analysis** – found: C, 77.18%; H, 8.03%; N, 4.53%; calculated for $C_{20}H_{25}NO_2$: C, 77.14%; H, 8.09%; N, 4.50%.

Experimental details

Hydrogen atoms were placed in geometrically idealized positions and refined using a riding model.

***Corresponding author: Da-Bin Shi,** School of Pharmaceutical Sciences, Zunyi Medical College, Zunyi 563000, People's Republic of China, e-mail: sdb007.student@sina.com
Mao-Yuan Zhang: School of Pharmaceutical Sciences, Zunyi Medical College, Zunyi 563000, People's Republic of China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N1	1.01666(11)	0.2618(3)	0.97156(9)	0.0501(4)
O1	0.84255(9)	−0.0313(2)	0.34469(7)	0.0597(4)
O2	0.88168(9)	−0.3656(2)	0.38274(7)	0.0585(4)
C1	0.87000(10)	−0.1570(3)	0.39652(10)	0.0434(4)
H1A	1.0528(15)	0.184(4)	1.0031(14)	0.077(7)*
H1B	0.9869(9)	0.314(4)	0.9972(13)	0.073(8)*
C2	0.85974(15)	−0.4383(4)	0.30118(11)	0.0688(6)
H2A	0.8069	−0.3860	0.2785	0.103*
H2B	0.8597	−0.5929	0.3000	0.103*
H2C	0.8980	−0.3846	0.2707	0.103*
C3	0.89356(9)	−0.1026(3)	0.48273(9)	0.0384(4)
C4	0.92722(10)	−0.2524(3)	0.53955(10)	0.0440(4)
H4	0.9367	−0.3921	0.5238	0.053*
C5	0.94677(11)	−0.1957(3)	0.61944(10)	0.0444(4)
H5	0.9696	−0.2981	0.6569	0.053*
C6	0.93304(9)	0.0114(3)	0.64506(9)	0.0375(4)
C7	0.89960(10)	0.1606(3)	0.58721(10)	0.0438(4)
H7	0.8899	0.3003	0.6027	0.053*
C8	0.88065(10)	0.1053(3)	0.50738(10)	0.0435(4)
H8	0.8590	0.2083	0.4697	0.052*
C9	0.95344(9)	0.0717(3)	0.73074(9)	0.0380(4)
C10	0.90406(10)	0.2071(3)	0.76505(10)	0.0412(4)
H10	0.8571	0.2593	0.7332	0.049*
C11	0.92201(9)	0.2680(3)	0.84515(9)	0.0387(4)
C12	0.99342(9)	0.1921(3)	0.89239(9)	0.0363(3)
C13	1.04383(9)	0.0498(3)	0.85984(9)	0.0366(4)
C14	1.02243(9)	−0.0070(3)	0.78004(9)	0.0388(4)
H14	1.0555	−0.1015	0.7585	0.047*
C15	1.12105(10)	−0.0351(3)	0.91120(10)	0.0434(4)
H15	1.1099	−0.0534	0.9654	0.052*
C16	1.18931(12)	0.1259(4)	0.91768(16)	0.0764(7)
H16A	1.2031	0.1466	0.8659	0.115*
H16B	1.2355	0.0725	0.9543	0.115*
H16C	1.1727	0.2607	0.9370	0.115*
C17	1.14694(13)	−0.2540(3)	0.88521(13)	0.0634(6)
H17A	1.1021	−0.3517	0.8791	0.095*
H17B	1.1902	−0.3085	0.9250	0.095*
H17C	1.1648	−0.2401	0.8350	0.095*
C18	0.86296(10)	0.4105(3)	0.87851(10)	0.0481(4)
H18	0.8851	0.4304	0.9356	0.058*
C19	0.78179(13)	0.3036(5)	0.87322(16)	0.0864(8)
H19A	0.7558	0.2927	0.8181	0.130*
H19B	0.7489	0.3879	0.9020	0.130*
H19C	0.7890	0.1621	0.8962	0.130*
C20	0.85654(19)	0.6319(4)	0.84090(16)	0.0891(8)
H20A	0.9093	0.6947	0.8469	0.134*
H20B	0.8228	0.7214	0.8669	0.134*
H20C	0.8334	0.6202	0.7850	0.134*

Comment

N-Heterocyclic carbenes (NHCs) are an important class of compounds that has found application in various fields of chemistry [7]. Several methods have been reported for the synthesis of NHCs since their discovery in the early 1990s [8]. Amines/anilines have emerged as versatile and useful building blocks in a variety of synthetic transformations, which can be generally designed as different NHCs [9].

The title compound consists of two substituted phenyl moieties. The dihedral angle between the planes of two aromatic rings is 38.7°. The bond lengths of C12–N1 and C1–O1 are 1.398(2) Å and 1.203(2) Å, respectively. And the bond lengths of C1–O2 and C2–O2 are 1.338(2) Å and 1.439(2) Å, respectively. As a result of the partial conjugation of the aromatic rings, the bond length of C6–C9 is 1.481(2) Å. The bond angle (C1–O2–C2) and (O1–C1–O2) are 116.90(17)° and 123.32(17)°, respectively. In the crystal packing, dipole-dipole and van der Waals interactions are effective besides hydrogen bonding. Bond lengths and bond angles within the molecular system are in agreement with the values reported [10].

Acknowledgements: We are grateful for financial support from National Natural Science Foundation of China (grant no. 21362047) and Science and Technology Foundation of Guizhou Province (grant no. QKHSYZ-2013-3061 and QKHJZ-2014-2175).

References

1. Bruker. APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2012).
2. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany (1997).
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
4. Meiries, S.; Nolan, S. P.: A new synthetic route to *p*-methoxy-2,6-disubstituted anilines and their conversion into N-heterocyclic carbene precursors. Synlett **25** (2014) 393–398.
5. Benjamin, W. E.; Veit, D. R.; Perkins, M. J.; Bain, E.; Scharnhorst, K.; McDowall, S.; Patrick, D. L.; Gilbertson, J. D.: Sterically engineered perylene dyes for high efficiency oriented fluorophore luminescent solar concentrators. Chem. Mater. **26** (2014) 1291–1293.
6. Shi, D.; Ren, Y.; Jiang, H.; Cai, B.; Lu, J.: Synthesis, structures, and properties of two three-dimensional metal-organic frameworks, based on concurrent ligand extension. Inorg. Chem. **51** (2012) 6498–6506.
7. Bugaut, X.; Glorius, F.: Organocatalytic umpolung: N-heterocyclic carbenes and beyond. Chem. Soc. Rev. **41** (2012) 3511–3522.
8. Slugovc, C.; Burtscher, D.; Stelzer, F.; Mereiter, K.: Thermally switchable olefin metathesis initiators bearing chelating carbenes: influence of the chelate's ring size. Organometallics **24** (2005) 2255–2258.
9. Mercs, L.; Albrecht, M.: Beyond catalysis: *N*-heterocyclic carbine complexes as components for medicinal, luminescent, and functional materials applications. Chem. Soc. Rev. **39** (2010) 1903–1912.
10. Lai, H. W. H.; Wiscons, R. A.; Zentner, C. A.; Zeller, M.; Rowsell, J. L. C.: Supramolecular assembly of tris(4-carboxyphenyl)arenes: relationship between molecular structure and solid-state catenation motifs. Cryst. Growth Des. **16** (2016) 821–833.