Kui Zhang and Da-Bin Shi*

Crystal structure of dimethyl 4,4′-((4R, 5R)-4,5-diphenylimidazolidine-1,3-diyl)dibenzoate, \( \text{C}_{31}\text{H}_{28}\text{N}_{2}\text{O}_{4} \)

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Abstract
\( \text{C}_{31}\text{H}_{28}\text{N}_{2}\text{O}_{4} \), monoclinic, \( P_{2}1 \) (no. 4), \( a = 10.2166(2) \) Å, \( b = 11.5327(2) \) Å, \( c = 11.6484(2) \) Å, \( \beta = 109.637(2) \)°, \( V = 1292.65(5) \) Å\(^3\), \( Z = 2 \), \( R_{gt}(F) = 0.0502 \), \( wR_{ref}(F^2) = 0.1312 \), \( T = 149.9(5) \) K.

CCDC no.: 2233528

The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Dimethyl 4,4′-((1R, 2R)-1,2-diphenylethane-1,2-diyl)bis(azanediyl)dibenzoate was prepared following a modified literature procedure [6]. A mixture of \( \text{Pd}_2(\text{dba})_3 \) (70 mg, 0.12 mmol) and racemic 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (200 mg, 0.3 mmol) in toluene (20 mL) was stirred at room temperature for 30 min under Ar atmosphere. To this mixture we added (1R, 2R)-1,2-diphenylethane-1,2-diamine (850 mg, 4.0 mmol), methyl 4-bromobenzoate (1.8 g, 8.2 mmol) and \( \text{Cs}_2\text{CO}_3 \) (2.6 g, 8.0 mmol), and the mixture was stirred at 110 °C for 48 h. The reaction mixture was filtered through a pad of celite and washed with toluene, and the resulting filtrate was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography to give dimethyl 4,4′-((1R, 2R)-1,2-diphenylethane-1,2-diyl)bis(azanediyl)dibenzoate (1.5 g 78%) as yellow solid.

Dimethyl 4,4′-((4R, 5R)-4,5-diphenyl-4,5-dihydro-1H-imidazole-1,3-diyl)dibenzoate, chloride salt was prepared following a modified literature procedure [7]. A solution of dimethyl 4,4′-((1R, 2R)-1,2-diphenylethane-1,2-diyl)bis(azanediyl))
Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

<table>
<thead>
<tr>
<th>Atom</th>
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<th>z</th>
<th>$U_{eq}$/$U_{iso}$</th>
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Table 2: (continued)

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</table>

Dibenzate (1.0 g, 2.2 mmol) in tetrahydrofuran (30 mL) was stirred for 5 min. Triethyl orthoformate (30 mL) was subsequently added followed by the dropwise addition of anhydrous HCl (4.0 M in dioxane, 10.0 mL). The reaction was stirred for 5 h at 70 °C and concentrated under vacuum. The residue was triturated with ethyl acetate and water until a solid separated. The solid was isolated by filtration and washed with cold ethyl acetate to afford the pure desired dimethyl 4,4’-(4R, 5R)-4,5-diphenyl-4,5-dihydro-1H-imidazole-1,3-diyl)dibenzoate, chloride salt (1.1 g, 90%) as a white crystalline powder.

Synthesis of the title compound. Dimethyl 4,4’-(4R, 5R)-4,5-diphenyl-4,5-dihydro-1H-imidazole-1,3-diyl)dibenzoate, chloride salt (1.0 g, 0.2 mmol) was dissolved in dry methanol (10 mL) and sodium borohydride (0.04 g, 1.0 mmol) was added under inert conditions. After 1 h of stirring at room temperature, the solvent was removed in vacuo and the crude product was purified by silica-gel column chromatography to give dimethyl 4,4’-(4R, 5R)-4,5-diphenylimidazolidine-1,3-diyl)dibenzoate (0.8 g 80% yield) as white solid. Crystals were obtained by slow evaporation of an ethanol solution at room temperature over a period of seven days. Elemental analysis – found: C, 75.68%; H, 5.79%; N, 5.58%; calculated for C$_{35}$H$_{28}$N$_{2}$O$_{4}$: C, 75.59%; H, 5.73%; N, 5.69%.

**Experimental details**

The absolute structure determination succeeded as the derived Flack parameter is found to be near zero [0.06(11) from 1850 selected quotients] using Parsons’ method [5].

**Comment**

Metal-organic frameworks (MOFs), assembled from metal ions or clusters and organic linkers via metal-ligand
coordination bonds, have drawn intense attention due to their well-defined structures and tailorable pore constructs, as well as great promise for a wide range of applications such as gas storage/separation [8, 9] and catalysis [10, 11]. Currently, the common combinations of linkers in MOFs are carboxylate ligands with different configurations. Here, we report a new carboxylate ligand precursor.

The asymmetric unit of the title structure contains one title molecule. In the crystal structure, bond lengths and bond angles within the molecular system are in agreement with the values reported [12]. The bond lengths of C31–N1 and C31–N2 are 1.447(3) Å and 1.444(4) Å, respectively. And the bond lengths of O1–C21 and O3–C29 are 1.202(4) Å and 1.187(5) Å, respectively. As a result of the conjugation of the benzene moiety and adjacent carbon-nitrogen bonds, the bond lengths of C15–N1 and C23–N2 are 1.379(3) Å and 1.376(3) Å respectively, which is shorter than that of typical C–N (1.47 Å). Furthermore, the bond lengths of C21–O2 and C29–O4 are 1.348(4) Å and 1.346(4) Å, respectively. The bond angles (C15–N1–C31) and (C23–N2–C31) are 122.3(2)° and 122.6(2)°, respectively.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References