



# Short Note Methyl-3-(3-hydroxy-3-(4-(piperidin-1-yl)phenyl)-prop-2enoyl)benzoate

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**Abstract:** The title compound was synthesized and characterized for the first time by <sup>1</sup>H, <sup>13</sup>C NMR, high-resolution mass spectra and single-crystal X-ray diffraction.

Keywords: 1,3-diketone; X-ray crystallography; hydrogen bond

# 1. Introduction

The growing interest in the design and synthesis of 1,3-diketones is, in particular, due to the great potential of these ligands as versatile building blocks for the construction of highly emissive metal complexes for application in organic light-emitting diodes (OLEDs) [1–11]. Aromatic  $\beta$ -diketones are also considered to be promising ligands for the creation of strong light-absorbing metal complexes for dye-sensitized solar cells [12–15]. This application requires the specific structure of diketones which should contain at least one carboxy- (or ester) group and electron-donating fragment(s) to give the resulting metal complexes robust light-harvesting characteristics. Such  $\beta$ -diketones are evidently asymmetric and, hence, they can be scarcely obtained via the common Claisen condensation. In this work, we synthesized an asymmetric aromatic 1,3-diketone (Figure 1) bearing the carboxymethyl group and the piperidine moiety under mild conditions and characterized the prepared ligand by a <sup>1</sup>H, <sup>13</sup>C {<sup>1</sup>H} NMR, high-resolution mass spectra, UV-vis spectroscopy and single-crystal X-ray diffraction.



Figure 1. Chemical structure of the title compound.

## 2. Results and Discussion

The title diketone was synthesized via the reaction of a benzotriazole amide of isophthalic acid monomethyl ester acting as the mild acylation agent with 1-(4-(piperidin-1yl)phenyl)ethanone (Scheme 1). The low yield of the product (10%) is likely a result of the side formation of a symmetrical 1,3-di-(3-carboxymethylphenyl)-propane-1,3-dione (see the <sup>1</sup>H NMR spectrum of the crude product in Supplementary Materials Figures S3–S5 and chemical structure of the side product) by a previously described intermolecular benzotriazole-mediated acylation/deacetylation process [16].



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Scheme 1. Preparation of methyl-3-(3-hydroxy-3-(4-(piperidin-1-yl)phenyl) prop-2-enoyl)benzoate.

The composition and structure of the  $\beta$ -diketone were identified by various spectroscopic techniques. The <sup>1</sup>H NMR spectrum (Figure S1, Supplementary Materials) shows a characteristic singlet of the OCH<sub>3</sub> group at 3.98 ppm while two multiples at 1.69 and 3.40 ppm with the relative intensities 6 and 4, respectively, arise from the protons of the piperidine ring; the aromatic protons appear at 6.91–8.60 ppm. The <sup>13</sup>C NMR spectrum consists of 18 individual signals consistent with the number of unique carbon atoms in the title compound (Figure S2). In the high-resolution mass spectrum, the dominant molecular ion peak corresponds to the [M + H]<sup>+</sup> ion.

The obtained diketone exists in enol form in the solution, as evidenced by its <sup>1</sup>H NMR spectrum containing two characteristic singlets at 6.82 and 17.15 ppm corresponding to the  $\alpha$ -methine proton and hydroxy-group of the enol, respectively. Single-crystal X-ray diffraction analysis revealed that the title compound exists in enol form in the solid state too.

The molecular structure of the enol is depicted in Figure 2. The conformation is nonplanar with interplanar angles between the substituted phenyl rings and the keto-enol plane ranging from  $3.77(4)^{\circ}$  to  $21.31(4)^{\circ}$ . The C9–O2 bond (1.2720(13) Å) is significantly shorter than the C11–O1 bond (1.3190(13) Å); that is in good agreement with the data from the Cambridge Structural Database (Version 5.43, March 2022, Cambridge, UK). Though there are a fairly large number of reports on crystal structures of symmetrical and asymmetrical  $\beta$ -diketones (more than 450 structures), analysis of the database shows that the vast majority of these compounds crystallizes in enol form and only 15 are pure diketones.



**Figure 2.** Molecular structure of the title enol. Displacement ellipsoids are shown at 50% probability level.

According to the database, in the structures of enols the intramolecular resonanceassisted hydrogen bonds impart short O···O distances (2.39–2.55 Å) [17]. The hydrogen atom shared between these oxygen atoms can be ordered, disordered by symmetry, as in dibenzoylmethane [18] and many other symmetrical  $\beta$ -diketones [19], or disordered with unequal occupancies (the most asymmetrical enols). In the case of the title compound, the H2 atom located from the difference Fourier map is closer to the O1 atom with the O1–H2 bond length of 1.07(2) Å, which lies within the expected range 0.76(4)–1.26(7) Å, according to the CSD (273 structures). Although the corresponding C–O–H angle is as small as  $103(3)^{\circ}$ , it falls within the range from 94 to  $112^{\circ}$ , which is common for this type of intramolecular hydrogen bonds. In the crystal, enol molecules are assembled by weak van der Waals interactions (Figure S7).

#### 3. Materials and Methods

## 3.1. General Comment

All commercially available reagents were at least reagent grade and used without further purification. Solvents were distilled and dried according to standard procedures. Benzotriazole amide of isophthalic acid monomethyl ester was previously prepared by the method described in the work [20].

<sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired at 25 °C on a Bruker Avance 400 instrument (Billerica, MA, USA) and chemical shifts were reported in ppm referenced to residual solvent signals. High resolution and accurate mass measurements were carried out using a Brukermicro-TOF-Q<sup>TM</sup> spectrometer (Billerica, MA, USA). The electronic absorption spectrum was measured on an OKB Spectr SF-2000 spectrophotometer (Saint Petersburg, Russia).

### 3.2. Synthesis

A suspension of MgBr<sub>2</sub>·Et<sub>2</sub>O (0.96 g, 3.7 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) benzotriazole amide (0.5 g, 1.8 mmol) was added and the mixture was sonicated for a minute. 1-(4-(piperidin-1-yl)phenyl)ethenone (0.3 g, 1.48 mmol) was added to the mixture and it was sonicated for a minute. *N*,*N*-Diisopropylethylamine (0.775 mL, 4.5 mmol) was added to the resulting suspension and the mixture was stirred at room temperature for 20 h. The reaction mixture was treated by 2 M HCl (30 mL) and vigorously stirred for 0.5 h. The organic layer was separated and the aqueous layer was extracted by CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The combined organic extracts were filtrated through paper followed by the evaporation of the solvent. The resulting oil was crystallized from CH<sub>3</sub>OH to give a yellow–brown powder, which was dried in vacuo and purified by column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane 1:10  $\rightarrow$  1:3 vol.). The powder containing ~70% of the symmetrical side product was dissolved in dichloromethane for preparative TLC (SiO<sub>2</sub>, ethyl acetate/hexane 1:5 vol.). The resulting solid containing ~30% of the side product was purified by column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane 5:1 vol.). Yield 0.054 g (10%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 1.69 (m, 6H, l + m + n), 3.40 (m, 4H, k + o), 3.98 (s, 3H, CH<sub>3</sub>), 6.82 (s, 1H, e), 6.91(d, J = 3.8 Hz, 2H, g + j), 7.57 (t, J = 7.8 Hz, 1H, c), 7.93 (d, J = 4.5 Hz, 2H, h + i), 8.16–8.20 (m, 2H, b + d), 8.60 (s, 1H, a), 17.15 (s, 1H, f).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.0 (m), 25.0 (l), 48.2 (k), 52.0 (OCH<sub>3</sub>), 91.7 (e), 113.1 (arom.), 123.3 (arom.), 127.5 (arom.), 128.4 (arom.), 129.0 (arom.), 130.1 (arom.), 130.8 (arom.), 132.13 (arom.), 135.9 (arom.), 154.0 (arom.), 166.2 (<u>C</u>OOCH<sub>3</sub>), 181.0 (C<sub>diketonate</sub>), 186.3 (C<sub>diketonate</sub>).

HRMS (ESI) m/z:  $[M + H]^+$  calcd for C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub> 366.1705, found 366.1706.

UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  326 nm ( $\epsilon$  = 9900 M<sup>-1</sup> cm<sup>-1</sup>), 338.8 nm ( $\epsilon$  = 10,300 M<sup>-1</sup> cm<sup>-1</sup>), 404.4 nm ( $\epsilon$  = 6400 M<sup>-1</sup> cm<sup>-1</sup>).

#### 3.3. Crystallography Details

Single crystals of the target enol were obtained by recrystallization from ethyl acetate/hexane mixture. Crystallographic data were collected on a Bruker D8 Venture diffractometer (at T = 100 K) using graphite monochromatized Mo–K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) using  $\omega$ -scan mode. Absorption correction based on the measurements of equivalent reflections was applied [21]. The structure was solved by direct methods and refined by full matrix least-squares on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms [22,23]. All hydrogen atoms were found from the difference Fourier map and refined freely. The crystallographic details are presented in Table S1 and the crystal packing is plotted in Figure S7. CCDC 2204554 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Crystal Data for C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub> (M = 365.41 g/mol): monoclinic, space group P2<sub>1</sub>/c (no. 14), a = 11.7425(6) Å, b = 11.3120(7) Å, c = 13.9594(8) Å,  $\beta$  = 106.159(2)°, V = 1780.99(18) Å<sup>3</sup>, Z = 4, T = 100 K,  $\mu$ (MoK $\alpha$ ) = 0.094 mm<sup>-1</sup>, D<sub>calc</sub> = 1.363 g/cm<sup>3</sup>, 34187 reflections measured (2.36°  $\leq 2\Theta \leq 28.27^{\circ}$ ), 4403 unique (R<sub>int</sub> = 0.0396, R<sub>sigma</sub> = 0.0239) which were used in all calculations. The final R<sub>1</sub> was 0.0379 (I > 2 $\sigma$ (I)) and wR<sub>2</sub> was 0.1069 (all data).

**Supplementary Materials:** The following are available online. Part 1. NMR spectroscopy and high-resolution mass-spectrometry data: Figures S1–S6; Part 2. X-ray crystallography: Table S1, Figure S7; Part 3. Optical data: Figure S8.

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