

Crystal Structure of Pyridin-4-ylmethyl 4-Nitrobenzoate, C₁₃H₁₀N₂O₄

James T. P. MATSHWELE,^{*,**†} Sebusi ODITSE,^{*†} Ofentse MAZIMBA,^{*} Florence NAREETSILE,^{***}
Lebogang G. JULIUS,^{***} and Dalitso KEITUMETSE^{***}

^{*}Department of Chemical and Forensic Science, Botswana International University of Science and Technology,
P/Bag 16 Palapye, Botswana

^{**}Department of Applied Sciences, Botho University, PO Box 501564, Gaborone, Botswana

^{***}Department of Chemistry, University of Botswana, P/Bag UB704, Gaborone, Botswana

The structure of pyridin-4-ylmethyl 4-nitrobenzoate was determined by the single-crystal X-ray diffraction method. The compound crystallized in a monoclinic system, $P2_1/n$, and the unit cell parameters are, $a = 9.981(2)$, $b = 12.347(3)$, $c = 10.161(3)\text{Å}$, $\beta = 101.450(9)$, $Z = 4$, $V = 1227.3(5)\text{Å}^3$. The crystal structure was solved by intrinsic phasing and refined to final values of $R1 = 0.0451$ and $wR2 = 0.1393$.

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Pyridine derivatives have attracted much attention because of their medicinal properties, such as antifungal, antibacterial, anti-inflammatory, antiviral, and antitumor activities.¹⁻⁷ Furthermore, the benzylation of these compounds may induce biological properties that makes it possible for ester group-containing compounds to act as prodrugs, and thus deliver the actual active group to the target biomolecule.^{8,9} The coordination of these types of ligands to certain metals has also shown enhanced medicinal properties. It was in this regard that influenced the synthesis of these types of pyridine derivatives. We wish to further coordinate them to metals and test for their bioactivity. However, this paper describes the crystal structure of an ester-bridged pyridyl compound that has a nitro moiety bound at the para position.

In this research 4-nitrobenzoic acid (2.80 g, 16.8 mmol) was mixed with 25 mL of dimethyl formamide. Potassium carbonate (2.40 g, 17.4 mmol) was then added to the resulting mixture before refluxing, and the mixture was stirred for 30 min with a dry calcium chloride drying tube connected to the reaction vessel. Then, to the refluxed white precipitate obtained, 4-chloromethyl pyridine (3.00 g, 18.3 mmol) dissolved in 25 mL dimethylformamide was added quickly before covering with a dry calcium chloride drying tube. The mixture was then refluxed overnight at 70°C. Afterwards, the maroon precipitate obtained was cooled and neutralized with 10 mL of 10% sodium

hydrogen carbonate, 40 mL distilled water and filtered under suction. It was washed again with cold distilled water. Off-white solid obtained was then air dried before characterization. The product was then recrystallized with methanol and golden rhombohedral crystals were obtained. Figure 1 shows the synthesized pyridin-4-ylmethyl 4-nitrobenzoate compound. The crystal and structure-refinement data are summarized in Table 1.

All hydrogen atoms were placed at geometrically calculated positions and included in the least-squares calculations using the riding-atom model. Their U_{iso} values were fixed at $1.2 U_{eq}$ of

Table 1 Crystal data and structure refinement details

| |
|---|
| Empirical formula: C ₁₃ H ₁₀ N ₂ O ₄ |
| Formula weight = 258.23 |
| Temperature = 293(2)K |
| Crystal system: monoclinic |
| Space group: $P2_1/n$ |
| $a = 9.981(2)\text{Å}$ |
| $b = 12.347(3)\text{Å}$ |
| $c = 10.161(3)\text{Å}$ |
| $\beta = 101.450(9)^\circ$ |
| $V = 1227.2(5)\text{Å}^3$ |
| $Z = 4$ |
| $\rho_{calc} = 1.398\text{ g/cm}^3$ |
| $\mu = 0.106\text{ mm}^{-1}$ |
| $F(000) = 536$ |
| Crystal size = $0.3 \times 0.1 \times 0.1\text{ mm}^3$ |
| 2θ range for data collection = 6.182 to 49.174° |
| Index ranges = $-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-11 \leq l \leq 11$ |
| Reflections collected = 11425 |
| Independent reflections = 2033 [$R_{int} = 0.0678$, $R_{sigma} = 0.0429$] |
| Data/restraints/parameters = 2033/0/172 |
| Goodness-of-fit on $F = 1.093$ |
| Final R indexes: $I > 2\sigma(I)$ $R_1 = 0.0425$, $wR_2 = 0.1050$ |
| Final R indexes [all data]: $R_1 = 0.0834$, $wR_2 = 0.1393$ |
| Largest diff. peak/hole: $0.17/-0.18$ |
| Measurement: Bruker D8-Quest |
| Program system: SHELXT2015 |
| Structure determination: SHELXT2015 |
| CCDC: 2091544 |

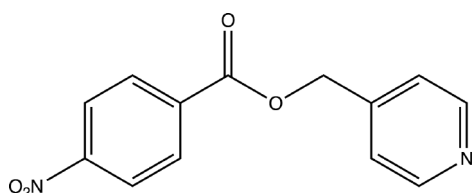


Fig. 1 Chemical diagram of the pyridin-4-ylmethyl 4-nitrobenzoate.

[†] To whom correspondence should be addressed.

E-mail: oditsites@biust.ac.bw (S. O.); james.matshwele@studentmail.biust.ac.bw (J. T. P. M.)

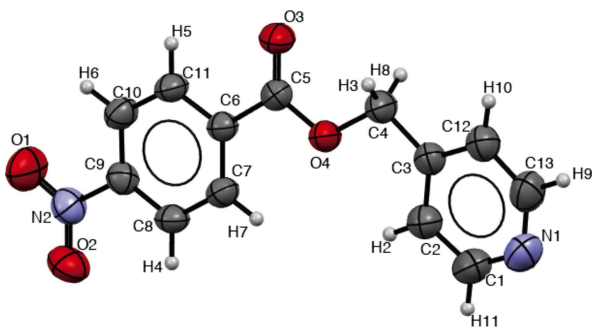


Fig. 2 ORTEP structure of pyridin-4-ylmethyl 4-nitrobenzoate, showing 50% probability ellipsoids.

Table 2 Selected bond angles

| Bond | Angle/° | Bond | Angle/° |
|---------------|-----------|---------------|-----------|
| C1-C2-C3-C4 | -179.6(3) | C8-C9-N2-O1 | -176.5(2) |
| C3-C4-O4-C5 | 177.8(2) | C10-C9-N2-O2 | -176.8(2) |
| C4-C3-C12-C13 | 179.7(3) | C12-C3-C4-O4 | -170.3(2) |
| C5-C6-C7-C8 | -177.6(2) | N2-C9-C10-C11 | 180.0(2) |
| C5-C6-C11-C10 | 177.5(2) | O3-C5-C6-C7 | -178.4(2) |
| C6-C5-O4-C4 | 175.0(2) | O4-C5-C6-C11 | -176.4(2) |
| C7-C8-C9-N2 | 179.8(2) | | |

their attaching carbon atoms.

The crystal structure of the reported molecule's analogue, 2-pyridyl 4-nitrobenzoate, has been reported before.¹⁰ The analogue was different in that it did not possess a methylene group that joins the ester to the pyridyl group. Our molecule was recovered as rhombohedral-shaped golden crystals. The crystal information of the molecules was similar. Also, the bond angles and lengths of the reported molecule were well within reported values and were similar to those of the analogue. They both crystallized in the monoclinic crystal system. The molecule transforms under the $P2_1/n$ space group while the analogue also transformed under the $P2_1/c$. As shown on the ORTEP structure on Fig. 2, the molecule's non hydrogen atoms and conjugated π system exhibits planarity with a benzene ring substituted with a nitro group and an ester group on the para position. The torsion angles on Table 2 and especially the bonds C3-C4-O4-C5 177.8(2), C6-C5-O4-C4 175.0° (2), C7-C8-C9-N2 179.8° (2),

C8-C9-N2-O1 -176.5° (2), C10-C9-N2-O2-176.8° (2), C12-C3-C4-O4 -170.3° (2), N2-C9-C10-C11 180.0° (2), O3-C5-C6-C7 -178.4° (2) and O4-C5-C6-C11 -176.4° (2) define this planarity. Some inter-molecular contacts are observed on the expanded unit cell, we observed contacts of the type C-H6...N1 2.530 Å [$x, -1+y, z$], C-H2...O2 2.553 Å [$1/2-x, -1/2+y, 1/2-z$], C-H10...O3 2.563 Å [$2-x, 1-y, 1-z$] and C-H4...O1 2.677 Å [$1/2-x, -1/2+y, 1/2-z$].

The CIF file is available as supporting material for all of the crystallographic information of the molecule. The file is freely available on the CSD database with the CCDC number 2091544.

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