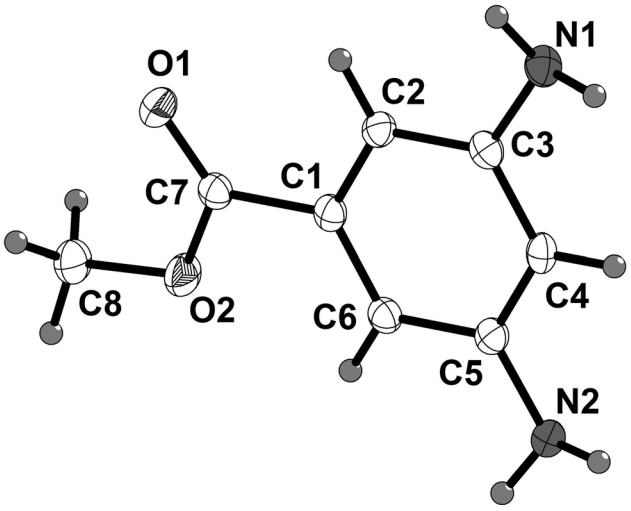
John M. Gardiner, James Raftery, Ian G. Beadham, Jannat N. Azarah, Mohammed Y. Abu-Foul, Adel M. Awadallah and Rami Y. Morjan*

The crystal structure of methyl 3,5-diaminobenzoate, $C_8H_{10}N_2O_2$



https://doi.org/10.1515/ncrs-2022-0485
Received October 5, 2022; accepted November 28, 2022; published online December 14, 2022

Abstract

$C_8H_{10}N_2O_2$, orthorhombic, *Pbca* (no. 61), a = 11.0571(2) Å, b = 8.1172(2) Å, c = 17.6080(4) Å, V = 1580.37(6) Å^3, Z = 8, $R_{gt}(F)$ = 0.0324, $wR_{ref}(F^2)$ = 0.0872, T = 100(2) K.

CCDC no.: 1519133

The molecular 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.

***Corresponding author: Rami Y. Morjan,** Department of Chemistry, Faculty of Science, The Islamic University of Gaza, Gaza, Gaza Strip, Palestine, E-mail: rmorjan@iugaza.edu.ps. https://orcid.org/0000-0003-4846-6419

John M. Gardiner and James Raftery, Department of Chemistry, School of Natural Sciences, Faculty of Science and Engineering, The University of Manchester, Manchester, M13 9PL, UK

Ian G. Beadham, Kingston University London, School of Life Sciences, Pharmacy and Chemistry, Kingston upon Thames, London, England, UK

Jannat N. Azarah, Mohammed Y. Abu-Foul and Adel M. Awadallah, Department of Chemistry, Faculty of Science, The Islamic University of Gaza, Gaza, Gaza Strip, Palestine

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.22 × 0.12 × 0.04 mm
Wavelength:	Cu *K*α radiation (1.54178 Å)
μ:	0.85 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	72.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7172, 1552, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1383
$N(param)_{refined}$:	126
Programs:	SHELX [1–3], Bruker [4]

Source of materials

To a solution of methyl 3,5-dinitrobenzoate (3.0 g, 13.3 mmol) [5, 6] in a 1:1 mixture of dry THF (100 mL) and dry ethanol (100 mL) was added 10% Pd–C (1.2 g, 11.3 mmol). The flask was degassed and purged with pure hydrogen for 45 min. The reaction was left stirring for 48 h. The reaction was filtered using Celite-545, and the solution was concentrated by evaporating most of the reaction solvent using a rotary evaporator. The residue was poured into *n*-hexane (150 mL). The product was filtered and the solvent was removed *in vacuo* to afford the title compound as brown powder (2.0 g, 91%). A sample of the title compound was dissolved in a mixture of DMSO/EtOH 10:1 *v*/*v* and left undisturbed. Unexpectedly the starting material was grown by slow evaporation of the solution over a period of seven days.

Experimental details

The structure was solved by Direct Methods. H atoms were included in calculated positions with C–H lengths of 0.95(CH), 0.99(CH_2) & 0.98(CH_3) Å; U_{iso}(H) values were fixed at 1.2U_{eq}(C) except for CH_3 where it was 1.5U_{eq}(C).

Comment

The title compound molecular structure is shown in the figure. It is a highly planar structure, in which the ester and aromatic ring both occupy the same plane, indicating

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.10499 (10)	0.86389 (13)	0.54508 (6)	0.0175 (3)
C2	0.19368 (10)	0.96328 (14)	0.57782 (6)	0.0181 (2)
H2	0.2675	0.9842	0.5519	0.022*
C3	0.17198 (10)	1.03160 (13)	0.64950 (6)	0.0176 (3)
C4	0.06231 (10)	1.00068 (13)	0.68634 (6)	0.0184 (3)
H4	0.0479	1.0478	0.7349	0.022*
C5	−0.02618 (10)	0.90202 (14)	0.65310 (6)	0.0181 (3)
C6	−0.00405 (10)	0.83186 (14)	0.58180 (6)	0.0183 (3)
H6	−0.0629	0.7630	0.5587	0.022*
C7	0.12825 (10)	0.79163 (14)	0.46850 (6)	0.0186 (3)
C8	0.05297 (12)	0.61452 (16)	0.37332 (7)	0.0275 (3)
H8A	0.0734	0.6985	0.3355	0.041*
H8B	−0.0229	0.5605	0.3589	0.041*
H8C	0.1179	0.5324	0.3757	0.041*
N1	0.26091 (10)	1.12400 (12)	0.68744 (6)	0.0220 (2)
N2	−0.13493 (9)	0.86971 (13)	0.69082 (6)	0.0213 (2)
O1	0.21725 (7)	0.81797 (11)	0.43036 (5)	0.0247 (2)
O2	0.03905 (8)	0.69125 (11)	0.44674 (5)	0.0268 (2)
H2A	−0.1597 (14)	0.952 (2)	0.7245 (9)	0.027 (4)*
H2B	−0.1931 (16)	0.838 (2)	0.6602 (10)	0.035 (4)*
H1B	0.2294 (14)	1.194 (2)	0.7217 (9)	0.032 (4)*
H1A	0.3134 (16)	1.179 (2)	0.6564 (10)	0.035 (4)*

conjugation of both the CH_3O lone pair and the aromatic system with the carbonyl. The X-ray structure revealed close contacts between both of the aromatic amino groups and nearby molecules in the crystal. One aromatic amine has intermolecular NH π-aromatic interactions with a neighboring aromatic system. This is evident from the close contacts between the aromatic NH and aromatic carbons ipso (2.628 Å) and ortho (2.692 and 2.776 Å) to the methyl ester. The other aromatic NH is involved in intermolecular hydrogen bonding with the methyl ester carbonyl oxygen at a distance of 2.265 Å. All bond lengths are in the expected ranges [7].

Acknowledgements: We would like to thank the world academy of sciences for the advancement of science in developing countries TWAS for their financial support. Funding for this research was provided by: the world academy of sciences for the advancement of science in developing countries TWAS (grant no. 16-490 RG/CHE/AF/AC_G – FR3240293296 to Adel M. Awadallah, Rami Y. Morjan); the world academy of sciences for the advancement of science in developing countries TWAS (scholarship no. 16-490 RG/CHE/AF/AC_G – FR3240293296 to Jannat N. Azzara).

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

Research funding: The world academy of sciences for the advancement of science in developing countries TWAS (grant no. 16-490 RG/CHE/AF/AC_G – FR3240293296 to Adel M. Awadallah, Rami Y. Morjan); the world academy of sciences for the advancement of science in developing countries TWAS (scholarship no. 16-490 RG/CHE/AF/AC_G – FR3240293296 to Jannat N. Azarah).

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

References

1. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Bruker. APEX2, SMART *(Version 5.630) and SAINT-Plus (Version 6.45A)*; Madison: WI, USA, 2009.
5. Gennas G., Talman V., Aitio O., Ekokoski E., Finel M., Tuominen R., Yli-Kauhaluoma J. Design, synthesis, and biological activity of isophthalic acid derivatives targeted to the C1 domain of protein kinase C. *J. Med. Chem.* 2009, *52*, 3969–3981.
6. Rzaczynska Z., Mrozek R., Lenik J., Sikorska M., Glowiak T. The crystal structures and vibrational spectra of 3,4-diaminobenzoic and 3,5-diaminobenzoic acids. *J. Chem. Crystallogr.* 2000, *30*, 519–524.
7. Rzaczyńska Z., Mrozek R., Lenik J., Sikorska M., Głowiak T. The crystal structures and vibrational spectra of 3,4-diaminobenzoic and 3,5-diaminobenzoic acids. *J. Chem. Crystallogr.* 2000, *30*, 519–524.