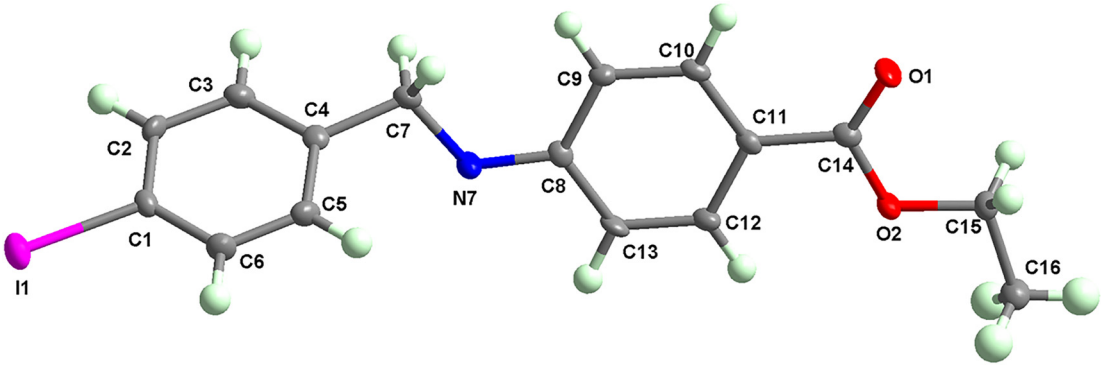
Chun-Jie Lv*

Synthesis and crystal structure of ethyl 4-((4-iodobenzyl)amino)benzoate, $C_{16}H_{16}INO_2$



https://doi.org/10.1515/ncrs-2022-0341
Received June 30, 2022; accepted July 20, 2022;
published online August 12, 2022

Abstract

$C_{16}H_{16}INO_2$, triclinic, $P\bar{1}$ (no. 2), a = 5.7004(2) Å, b = 6.8909(3) Å, c = 19.6509(8) Å, α = 100.035(4)°, β = 94.465(3)°, γ = 99.447(4)°, V = 745.27(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0321, $wR_{ref}(F^2)$ = 0.0595, T = 100.15 K.

CCDC no.: 2191548

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.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.13 × 0.11 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.15 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	29.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12605, 3637, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3228
$N(param)_{refined}$:	182
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of material

The title compound was prepared according to the following synthetic protocol. A solution of ethyl *p*-aminobenzoate (165 mg, 1.0 mmol), *p*-toluenesulfonic acid monohydrate 100 mg and *p*-iodobenzaldehyde (232 mg, 1.3 mmol) in dry toluene (20 mL) were heated at reflux temperature under nitrogen atmosphere for 24 h. The mixture was cooled to room temperature and filtered. The filtrate was washed with 5% aqueous sodium hydroxide and water, and dried over anhydrous magnesium sulfate. The crude product was purified on a silica-gel column using a mixture of petroleum ether and ethyl acetate, yielding light yellow solid (yield: 50%). Structural analysis: **^{1}H NMR** (300 MHz, $CDCl_3$) data δ 7.88 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 4.55 (br, 1H), 4.37 (s, 1H), 4.33 (q, J = 3.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) data δ 166.70, 151.28, 138.16, 137.81, 131.49, 129.19, 119.42, 111.72, 92.71, 60.23, 47.13, 14.42. **IR** cm^{-1} KBr data: 3350.10 cm^{-1}, 2959.14 cm^{-1}, 1720.70 cm^{-1}, 1599.88 cm^{-1}. The yellow crystals of the title compound were obtained by slow evaporation of dichloromethane/hexane at room temperature and the suitable single crystal was studied by X-ray diffraction method. **Elemental analysis:** Calculated for $C_{16}H_{16}INO_2$: C, 50.41%; H, 4.23%; I, 33.29%; N, 3.67%; O, 8.39%; found: C, 50.36%; H, 4.25%; I, 33.26%; N, 3.72%; O, 8.35%.

Experimental details

Coordinates of hydrogen atoms were refined using «riding» model with U_{iso} = n U_{eq} of the parent atom, where n = 1.5 for

***Corresponding author: Chun-Jie Lv**, Food and Pharmacy College, XuChang University, XuChang 461002, Henan Province, P. R. China, E-mail: lvchunjie1023@163.com. https://orcid.org/0000-0002-9164-8560

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
I1	0.85670 (3)	1.28814 (3)	0.03950 (2)	0.02411 (7)
O1	−0.2362 (3)	−0.1326 (3)	0.34685 (10)	0.0232 (4)
O2	0.1162 (3)	−0.0661 (3)	0.41345 (9)	0.0178 (4)
N1	0.3195 (4)	0.6593 (3)	0.25689 (11)	0.0195 (5)
H1	0.469123	0.716498	0.271005	0.023*
C1	0.6437 (4)	1.1100 (4)	0.09668 (13)	0.0160 (6)
C2	0.4552 (5)	1.1815 (4)	0.12674 (14)	0.0188 (6)
H2	0.423430	1.310076	0.122363	0.023*
C3	0.3136 (5)	1.0623 (4)	0.16330 (14)	0.0197 (6)
H3	0.184511	1.110837	0.184204	0.024*
C4	0.3561 (4)	0.8733 (4)	0.17010 (12)	0.0154 (5)
C5	0.5483 (4)	0.8069 (4)	0.13997 (14)	0.0190 (6)
H5	0.580953	0.678689	0.144551	0.023*
C6	0.6936 (5)	0.9233 (4)	0.10338 (13)	0.0195 (6)
H6	0.824808	0.876146	0.083264	0.023*
C7	0.1887 (4)	0.7410 (4)	0.20621 (13)	0.0176 (6)
H7A	0.077757	0.820273	0.229591	0.021*
H7B	0.092071	0.630034	0.171233	0.021*
C8	0.2243 (4)	0.4977 (4)	0.28437 (12)	0.0146 (5)
C9	−0.0148 (4)	0.3965 (4)	0.26629 (13)	0.0148 (5)
H9	−0.119723	0.444715	0.235962	0.018*
C10	−0.0966 (4)	0.2270 (4)	0.29269 (12)	0.0160 (6)
H10	−0.256591	0.158382	0.279246	0.019*
C11	0.0514 (4)	0.1551 (4)	0.33860 (12)	0.0143 (5)
C12	0.2870 (4)	0.2599 (4)	0.35801 (13)	0.0168 (6)
H12	0.389284	0.214439	0.389926	0.020*
C13	0.3719 (4)	0.4259 (4)	0.33186 (13)	0.0171 (6)
H13	0.531910	0.493835	0.345763	0.021*
C14	−0.0409 (4)	−0.0264 (4)	0.36521 (13)	0.0160 (6)
C15	0.0422 (5)	−0.2424 (4)	0.44325 (13)	0.0184 (6)
H15A	−0.001088	−0.363691	0.406258	0.022*
H15B	−0.097892	−0.227187	0.469165	0.022*
C16	0.2545 (5)	−0.2585 (4)	0.49168 (14)	0.0232 (6)
H16A	0.389091	−0.279772	0.464886	0.035*
H16B	0.211790	−0.371648	0.515146	0.035*
H16C	0.300278	−0.134442	0.526419	0.035*

hydrogen atoms of the methyl group and n = 1.2 for other hydrogen atoms.

Comment

Diarylamines are important building blocks in organic synthesis and are present as privileged structures innumerous pharmaceuticals and biologically active compounds. Due to the importance to medicinal chemistry, many methods exist for diarylamine synthesis, with transition metal-catalyzed C–N bond formation being especially prominent in recent years [5–8]. Up to date, there are only a few reports on diarylamines compounds especially their crystal structures [9–11].

There is one molecule in the asymmetric unit of the title structure which is shown in the figure. The p-methyliodophenyl group is attached to the 4-position of the ethyl benzoate. The C–N bond distance is 1.443(3) Å for C7 N1, which is normal for arylamine. The three bond angles around the amino group are 123.8(2)° for C7—N1—C8, 111.2(2)° for C4—C7—N1 and 119.0(2)° for N1—C8—C13, respectively. The dihedral angel between the benzene rings is 57.7(8)°. Molecules are linked by N—H ⋯ O hydrogen bonds to form one-dimensional chain-like supramolecular structure. These chains are linked by C—H–π interactions with the distance of 2.771 Å for hydrogen (H3) atom to the nearest carbon (C9) atom.

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

Research funding: This work was supported by Fundamental Research Funds for the Xuchang University (No: 2022YB032).

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

References

1. Oxford Diffraction Ltd *CrysAlis^{PRO}*; Oxford Diffraction Ltd: Abingdon, Oxfordshire, England, 2006.
2. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND*. Visual Crystal Structure Information System. Ver. 4.0; Crystal Impact: Bonn, Germany, 2015.
5. Ruiz-Castillo P., Buchwald S. L. Applications of palladium-catalyzed C–N cross-coupling reactions. *Chem. Rev.* 2016, *116*, 12564–12649.
6. Chen J. Q., Li J. H., Dong Z. B. A review on the latest progress of chan-lam coupling reaction. *Adv. Synth. Catal.* 2020, *362*, 3311–3331.
7. Sambiagio C., Marsden S. P., Blacker A. J., McGowan P. C. Copper catalysed Ullmann type chemistry: from mechanistic aspects to modern development. *Chem. Soc. Rev.* 2014, *43*, 3525–3550.
8. Thomas S., Jonathan M. L., Sam B., Michael F. G. Diarylamine synthesis via desulfifinylative smiles rearrangement. *Org. Lett.* 2022, *24*, 1132–1135.
9. Wang Z. S., Chen Y. B., Zhang H. W., Sun Z., Zhu C., Ye L. W. Ynamide smiles rearrangement triggered by visible-light-mediated regioselective ketyl-ynamide coupling: rapid access to functionalized indoles and isoquinolines. *J. Am. Chem. Soc.* 2020, *142*, 3636–3644.
10. Yan J., Cheo H. W., Teo W. K., Shi X., Wu H., Idres S. B., Deng L. W., Wu J. A radical smiles rearrangement promoted by neutral eosin Y as a direct hydrogen atom transfer photocatalyst. *J. Am. Chem. Soc.* 2020, *142*, 11357–11362.
11. Alpers D., Cole K. P., Stephenson C. R. J. Visible light mediated aryl migration by homolytic C–N cleavage of aryl amines. *Angew. Chem. Int. Ed.* 2018, *57*, 12167–12170.