Crystal structure of (2*S*,3*R*)-2-[hydroxy(3-nitrophenyl)methyl]-cyclopentanone, C₁₂H₁₃NO₄

Ping Liu^{*,†}, Lian Zhaoxun[†] and Yuhuan Chen[‡]

[†] Henan Institute of Science and Technology, School of Chemistry and Chemical Engineering, Xinxiang, Henan 453003, P. R. China

[‡] Hebei University of Technology, School of Chemical Engineering and Technology, Tianjin 300130, P. R. China

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Abstract

C₁₂H₁₃NO₄, orthorhombic, *P*2₁2₁2₁ (no. 19), *a* = 5.3307(1) Å, *b* = 7.0082(1) Å, *c* = 29.9491(6) Å, *V* = 1118.9 Å³, *Z* = 4, *R*_g(*F*) = 0.054, *wR*_{ref}(*F*²) = 0.215, *T* = 150 K.

Source of material

3-Nitrobenzaldehyde (76 mg, 0.5 mmol) and cyclopentanone (0.5 mL) was added to a solution of L-tryptophan (30.6 mg, 0.15 mmol) and pure water (0.5 mL) at room temperature. The mixture was stirred, monitored by TLC. After 12 h, the mixture was quenched with the saturated aqueous NaHCO₃ solution and extracted by ethyl acetate (3 × 15 mL). The solvent was removed in vacuo to yield the crude product. Purification by silica gel chromatography using 100 ~ 200 mesh ZCX II eluted by hexane/ethyl acetate (3:1, v/v) gave the yellow solid (81 mg, yield 69 %). The crystalline compound was obtained through the slow volatilization of ethyl acetate.

Discussion

The direct asymmetric aldol reaction is one of the most important C—C bond-forming reactions [1]. Thus, it is not surprising that a large number of catalysts and methods have been developed to achieve efficient adducts with high diastereo- and enantioselectivities [2–4]. In nature, class I or class II aldolases can catalyze the aldol reaction. The previous reports have demonstrated that proline and its derivatives have been utilized as catalysts for aldol reactions with high diastereo- and enantioselectivities in water under special design conditions [5–7], and primary and secondary amines are capable of catalyzing intermolecular aldol reactions under physiological conditions [8,9]. Recently, acyclic amino acids were reported to be able to catalyze direct asymmetric aldol reactions in organic solvents [10]. Acyclic amino acids can catalyze the direct stereoselective aldol reaction in water micelles [11].

The asymmetric unit contains one independent title molecule, which displays the absolute molecular conformation being a (2*S*,3*R*) isomer. The Flack parameter was refined as 0.4(4) indicating a possible racemic twin of about 40 %. In the crystal structure, the distance of O2—C9 is 1.219(4) Å, which shows the feature of typical C=O bond. The distance of O1—C7 is 1.425(3) Å, indicating single-bond character. Other bond lengths and angles are within ranges as reported [12]. The nitro group is almost coplanar with the corresponding benzene ring with mean deviation from plane being 0.027 Å. The most striking feature of the crystal structure is the interesting arrangement of the title molecules, interconnected to form a chain along [100] by weak intermolecular C—H...O hydrogen bonds. C4—H4A and C12—H12A are donors and O3 and O4 are H-bond acceptors. These intramolecular O—H...O hydrogen bonds consolidate the crystal packing.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.20 × 0.29 × 0.38 mm
Wavelength:	Cu K _α radiation (1.54178 Å)
μ:	8.85 cm ^{−1}
Diffraction, scan mode:	Bruker APEXII CCD, φ/ω
2θ _{max} :	152.74°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	3970, 2069
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1911
<i>N</i> (<i>param</i>) _{refined} :	155
Programs:	SHELXS-97 [13], SHELXL-97 [14], SHELXTL [15]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	4a	1.0471	1.0064	0.0803	0.069
H(2A)	4a	0.5569	1.1338	0.1281	0.048
H(8A)	4a	0.6704	0.7891	0.0616	0.045
H(6A)	4a	0.7090	0.6316	0.1871	0.057
H(5A)	4a	0.3781	0.6752	0.2356	0.060
H(7A)	4a	1.0158	0.7778	0.1341	0.047
H(11A)	4a	0.7248	0.2714	0.0511	0.057
H(11B)	4a	0.6070	0.4402	0.0232	0.057
H(10A)	4a	1.1188	0.3882	0.0445	0.059
H(10B)	4a	1.0082	0.4654	−0.0009	0.059
H(12A)	4a	0.5079	0.5287	0.0957	0.054
H(12B)	4a	0.7712	0.4613	0.1140	0.054
H(4A)	4a	0.1361	0.9510	0.2318	0.056

* Correspondence author (e-mail: liuping96@sohu.com)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	4a	0.9594(4)	1.0217(3)	0.10251(6)	0.049(1)	0.0357(9)	0.053(1)	−0.0037(9)	0.0040(8)	−0.0005(7)
O(2)	4a	1.1872(4)	0.7815(3)	0.04011(7)	0.044(1)	0.055(1)	0.052(1)	−0.007(1)	0.0065(9)	0.0017(9)
C(2)	4a	0.5221(5)	1.0408(4)	0.14942(8)	0.041(1)	0.039(1)	0.038(1)	−0.005(1)	0.002(1)	0.001(1)
O(4)	4a	−0.0044(5)	1.2563(4)	0.20241(8)	0.062(1)	0.067(1)	0.059(1)	0.009(1)	0.020(1)	−0.007(1)
N(1)	4a	0.1774(5)	1.2413(4)	0.17743(8)	0.049(1)	0.042(1)	0.051(1)	−0.004(1)	0.007(1)	−0.0080(9)
O(3)	4a	0.2359(5)	1.3631(3)	0.15033(9)	0.058(1)	0.038(1)	0.086(2)	0.000(1)	0.018(1)	0.007(1)
C(8)	4a	0.7946(5)	0.7172(4)	0.07892(8)	0.040(1)	0.033(1)	0.041(1)	−0.002(1)	−0.002(1)	0.0016(9)
C(6)	4a	0.6107(6)	0.7408(4)	0.18472(9)	0.056(2)	0.044(1)	0.043(1)	−0.000(1)	−0.002(1)	0.005(1)
C(5)	4a	0.4134(6)	0.7677(4)	0.21421(9)	0.061(2)	0.050(1)	0.039(1)	−0.005(1)	0.003(1)	0.007(1)
C(7)	4a	0.8768(5)	0.8409(4)	0.11854(8)	0.043(1)	0.033(1)	0.043(1)	−0.000(1)	−0.001(1)	0.0023(9)
C(3)	4a	0.3262(6)	1.0662(4)	0.17964(8)	0.045(1)	0.042(1)	0.040(1)	−0.006(1)	−0.001(1)	−0.004(1)
C(11)	4a	0.7307(6)	0.4077(4)	0.04569(9)	0.058(2)	0.037(1)	0.048(1)	−0.002(1)	−0.005(1)	−0.001(1)
C(9)	4a	1.0158(6)	0.6719(4)	0.04830(8)	0.043(1)	0.043(1)	0.039(1)	0.002(1)	−0.002(1)	0.004(1)
C(10)	4a	0.9918(6)	0.4697(4)	0.0313(1)	0.053(2)	0.045(1)	0.050(1)	0.007(1)	−0.001(1)	−0.005(1)
C(12)	4a	0.6855(6)	0.5204(4)	0.08896(8)	0.054(2)	0.037(1)	0.042(1)	−0.006(1)	−0.002(1)	0.001(1)
C(4)	4a	0.2685(6)	0.9317(4)	0.21204(8)	0.047(1)	0.057(2)	0.037(1)	−0.009(1)	0.002(1)	−0.004(1)
C(1)	4a	0.6648(6)	0.8752(4)	0.15138(8)	0.047(1)	0.037(1)	0.037(1)	−0.004(1)	−0.002(1)	−0.0021(9)

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