Crystal structure of *E*-benzaldehyde *O*-benzoyloxime, C₁₄H₁₁NO₂

O. Altınbaş^I, H. A. Dondas^{*,II}, H. Arslan^{*,I}, N. Külçü^I and C. Killner^{III}^I Mersin University, Faculty of Arts and Sciences, Department of Chemistry, 33343 Mersin, Turkey^{II} Mersin University, Faculty of Pharmacy, Department of Chemistry, 33169 Mersin, Turkey^{III} University of Leeds, School of Chemistry, LS2 9JT Leeds, UK

Received April 15, 2004, accepted and available on-line September 17, 2004; CCDC no. 1267/1309

Abstract

C₁₄H₁₁NO₂, orthorhombic, *P*2₁2₁2₁ (no. 19), *a* = 5.9386(2) Å, *b* = 8.8513(3) Å, *c* = 21.5491(9) Å, *V* = 1132.7 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.053, *wR*_{ref}(*F*²) = 0.140, *T* = 150 K.

Source of material

The compound was prepared by a novel procedure that not reported in the literature before. Thus a solution of *E*-benzaldehyde (2.5 mmol) and NaH (100 mg, 60 % dispersion in mineral oil, 2.5 mmol) in dry tetrahydrofuran (30 ml), were stirred for 20 min at room temperature under nitrogen. Then benzoylisothiocyanate (2.6 mmol) was added to the reaction mixture over 15 min and the resulting solution stirred at room temperature for another 3 h. THF was removed under reduced pressure, water (25 ml) added and the mixture extracted with chloroform (5 × 20 ml). The combined organic layer was dried (MgSO₄), the solvent removed under reduced pressure, followed by crystallization from petroleum ether (b.p. 60–80 °C)/ethyl acetate giving the title compound as colorless fragment (yield 89 %, m.p. 83–85 °C). Elemental analysis: found – C, 74.0 %, H, 5.0 %; N, 6.2 %; calc. for C₁₄H₁₁NO₂ – C, 74.7 %, H, 4.9 %; N, 6.2%. ¹H NMR, ¹³C NMR, MS and IR data are available in the CIF file.

Discussion

Most of the oxime compounds played an important role as model compounds in the elucidation of some biological and biochemical mechanisms. One of these compounds is *E*-benzaldehyde *O*-benzoyloxime. In previous studies, *E*-benzaldehyde *O*-benzoyloxime was prepared by the reactions of *E*-benzaldehyde with benzoylchloride [1]. Also, elimination reactions of (*E*)- and (*Z*)-benzaldehyde *O*-benzoyloxime with 1,8-diazabicyclo[5.4.0]undec-7-ene in MeCN had been investigated kinetically. The reactions of *O*-benzoyloxime were second order and exhibit substantial values of Hammett ρ and k_H/k_D values, and an E2 mechanism was evident. We found no report in the literature for the crystal structure of *E*-benzaldehyde *O*-benzoyloxime.

The most of the essential bond lengths of the title compound, *d*(C1—O1) = 1.203(3) Å, *d*(C1—O2) = 1.354(3) Å, *d*(N1—O2) = 1.441(2) Å and *d*(C2—N1) = 1.273(3) Å, are the same as the related bond lengths of other oxime and benzoyl compounds [2]. Within the experimental errors all these bond lengths correspond with literature data [3]. However, the N1—O2 bond length, 1.441(2) Å, is slightly longer than the N—O single bond length (1.420 Å [3]), but approximately equal to the value obtained in [4]. The C2—N1 bond distance, 1.273(3) Å, is slightly shorter than a regular C=N double bond length (1.28 Å [3]) and agrees with that found for 2,2-dimethyl-6-nitro-3,4-dihydro-2*H*-benzo[*b*]pyran-4-one *O*-benzoyloxime [5]. The *O*-benzoyloxime group structure data and all the other bond lengths and angles of the title structure fall within the expected range.

Table 1. Data collection and handling.

Crystal:	colorless fragment, size 0.19 × 0.24 × 0.26 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ:	0.89 cm ^{−1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
2θ _{max} :	52°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	13912, 2204
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1946
<i>N</i> (<i>param</i>) _{refined} :	199
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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(2)	4 <i>a</i>	1.342(5)	0.682(3)	0.090(1)	0.060(7)
H(4)	4 <i>a</i>	1.582(4)	0.853(2)	0.147(1)	0.041(5)
H(5)	4 <i>a</i>	1.659(5)	1.015(3)	0.228(1)	0.052(6)
H(6)	4 <i>a</i>	1.403(5)	1.055(3)	0.306(1)	0.067(7)
H(7)	4 <i>a</i>	1.068(4)	0.930(2)	0.308(1)	0.045(6)
H(8)	4 <i>a</i>	0.962(5)	0.766(3)	0.222(1)	0.059(7)
H(10)	4 <i>a</i>	0.483(5)	0.520(3)	−0.047(1)	0.058(7)
H(11)	4 <i>a</i>	0.457(5)	0.351(3)	−0.134(1)	0.068(7)
H(12)	4 <i>a</i>	0.762(4)	0.195(2)	−0.156(1)	0.040(5)
H(13)	4 <i>a</i>	1.090(5)	0.194(3)	−0.093(1)	0.052(6)
H(14)	4 <i>a</i>	1.099(4)	0.374(2)	−0.013(1)	0.042(6)

* Correspondence authors (e-mail: yakdas25@mersin.edu.tr, arslanh@mersin.edu.tr)

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
N(1)	4a	1.0075(3)	0.6614(2)	0.11295(7)	0.054(1)	0.0442(9)	0.0424(9)	−0.0035(9)	0.0011(8)	−0.0060(7)
O(1)	4a	0.6602(3)	0.6652(2)	0.03938(8)	0.048(1)	0.073(1)	0.067(1)	0.0119(9)	0.0017(8)	−0.0177(8)
O(2)	4a	1.0025(3)	0.5654(1)	0.05895(6)	0.0490(9)	0.0415(7)	0.0481(8)	0.0007(7)	−0.0046(7)	−0.0065(6)
C(1)	4a	0.8060(4)	0.5754(2)	0.02741(9)	0.043(1)	0.045(1)	0.045(1)	−0.004(1)	0.0050(9)	0.0034(8)
C(2)	4a	1.2097(4)	0.7039(2)	0.12185(9)	0.043(1)	0.039(1)	0.045(1)	0.0044(9)	0.0009(9)	0.0016(8)
C(3)	4a	1.2656(4)	0.7992(2)	0.17564(9)	0.039(1)	0.0327(9)	0.048(1)	0.0031(8)	−0.0011(9)	0.0033(8)
C(4)	4a	1.4735(4)	0.8714(2)	0.1780(1)	0.040(1)	0.043(1)	0.053(1)	0.0045(9)	0.003(1)	0.0050(9)
C(5)	4a	1.5246(4)	0.9672(2)	0.2264(1)	0.040(1)	0.045(1)	0.061(1)	−0.005(1)	−0.006(1)	0.004(1)
C(6)	4a	1.3709(4)	0.9900(2)	0.2740(1)	0.052(1)	0.038(1)	0.054(1)	−0.0024(9)	−0.007(1)	−0.0039(9)
C(7)	4a	1.1647(4)	0.9175(2)	0.2725(1)	0.051(1)	0.041(1)	0.049(1)	−0.000(1)	0.005(1)	−0.0012(8)
C(8)	4a	1.1116(4)	0.8213(2)	0.2238(1)	0.043(1)	0.038(1)	0.049(1)	−0.0032(9)	0.0004(9)	−0.0003(8)
C(9)	4a	0.7983(4)	0.4641(2)	−0.02409(9)	0.041(1)	0.041(1)	0.043(1)	−0.007(1)	0.0033(8)	0.0052(8)
C(10)	4a	0.6038(4)	0.4583(3)	−0.0605(1)	0.042(1)	0.046(1)	0.051(1)	−0.004(1)	0.0038(9)	0.0064(9)
C(11)	4a	0.5924(4)	0.3574(3)	−0.1099(1)	0.046(1)	0.054(1)	0.050(1)	−0.011(1)	−0.006(1)	0.0059(9)
C(12)	4a	0.7715(4)	0.2631(2)	−0.1228(1)	0.057(1)	0.046(1)	0.045(1)	−0.010(1)	0.001(1)	−0.0055(9)
C(13)	4a	0.9634(4)	0.2676(2)	−0.0865(1)	0.047(1)	0.044(1)	0.053(1)	−0.001(1)	0.003(1)	−0.0019(9)
C(14)	4a	0.9771(4)	0.3672(2)	−0.0370(1)	0.040(1)	0.045(1)	0.047(1)	−0.0057(9)	−0.002(1)	0.0022(8)

References

1. Cho, B. R.; Chung, H. S.; Cho, N. S.: Elimination reaction of (*E*)- and (*Z*)-Benzaldehyde *O*-Benzoyloximes. Transition State Differences for the *Syn*- and *Anti*-Eliminations forming nitriles. *J. Org. Chem.* **63** (1998) 4685–4690.
2. Altınbas, O.: Reaction of oximes and pyrrolidine with benzoylisothiocyanate. MS Thesis. Mersin University, Mersin, Turkey 2004.
3. Allen, F. H.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R.: Typical Interatomic Distances: Organic Compounds. In: *International Tables for Crystallography. Vol. C. Mathematical, physical and chemical tables* (Eds. A. J. C. Wilson, E. Prince), pp. 782–803. Kluwer Academic Publishers, Dordrecht, The Netherlands 1999.
4. Schomaker, V.; Stevenson, D. P.: Some Revisions of the Covalent Radii and the Additivity Rule for the Lengths of Partially Ionic Single Covalent Bonds. *J. Am. Chem. Soc.* **63** (1941) 37–40.
5. Yang, Q.-C.; Li, H.-M.; Tang, Y.-Q.; Huang, W.-L.: 2,2-Dimethyl-6-nitro-3,4-dihydro-2*H*-benzo[*b*]pyran-4-one *O*-benzoyloxime. *Acta Crystallogr. C52* (1996) 2920–2922.
6. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
7. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.