

C2—O1—C9	108.6 (3)	C6—C7—C8	114.5 (4)
O11—C2—O1	120.5 (3)	C6—C7—C10	121.4 (4)
O11—C2—C3	131.5 (5)	C8—C7—C10	124.1 (4)
O1—C2—C3	108.0 (4)	C3—C8—C7	122.7 (3)
C4—C3—C8	122.3 (3)	C3—C8—C9	108.2 (3)
C4—C3—C2	129.7 (4)	C7—C8—C9	129.1 (4)
C8—C3—C2	107.9 (4)	O12—C9—O1	118.6 (4)
C3—C4—C5	117.0 (4)	O12—C9—C8	134.1 (4)
C4—C5—C6	120.5 (4)	O1—C9—C8	107.3 (4)
C7—C6—C5	123.0 (3)		

The amplitude of the Lehman & Larsen (1974) scans is given by $(0.55 + 0.55 \tan \theta)^\circ$. A decrease in the intensity of the standard reflection of about 55% was found during the data collection time and a correction for this decay was included in the data reduction procedure. Data were also corrected for Lorentz and polarization effects but not for absorption. All the calculations were performed on a 466DE Dell computer with the *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreotti, 1987) package. Refinement was on F^2 for all reflections except for 3 reflections with very negative F^2 or flagged by the user for potential systematic errors. The unreliable determination of the Flack (1983) parameter arose because of the severe decay suffered by the crystal. It was not possible to acquire the anomalous-diffraction data which could have improved the determination.

Data collection: Belletti, Cantoni & Pasquinelli (1992). Cell refinement: Belletti, Cantoni & Pasquinelli (1992). Data reduction: Belletti, Cantoni & Pasquinelli (1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl 3-(3-Bromo-4-hydroxyphenyl)-2(E)-(hydroxyimino)propanoate

NIGAM P. RATH, TODD R. BOEHLW AND
CHRISTOPHER D. SPILLING

Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121, USA

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Abstract

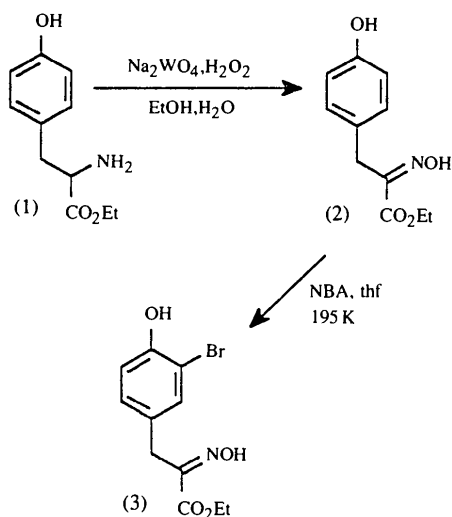
The crystal structure determination of the title compound, C₁₁H₁₂BrNO₄, m.p. 408.5–409.3 K, shows the oxime geometry to be *E* (*trans*). In the crystal structure, two molecules form a head-to-tail hydrogen-bonded cyclic dimer, with the hydrogen bonds between the phenol H atom of one molecule and the carboxylate O atom of the other. The dimers are hydrogen bonded *via* the oximes to form a repeating chain.

Comment

Over the last twenty-five years several metabolites of tyrosine have been isolated from a variety of marine sponges of the order Verongida (Berquist & Wells, 1983; Ireland *et al.*, 1989). In most cases metabolism involves bromination of the tyrosine aromatic ring and oxidation of the amine to an oxime. The tyrosine oximes are then further metabolized to form spirocyclic isoxazolines, biphenyl ethers and semiquinols. Recently, we began to investigate a biomimetic synthesis of these metabolites from tyrosine, including methods for oxidation of the amine to the corresponding oxime.

Treatment of the tyrosine ethyl ester (1) with 1 equivalent of sodium tungstate and 10 equivalents of hydrogen peroxide in aqueous ethanol (Kahr & Berther, 1960) gave the corresponding oxime (2) in an 85% yield as a single geometric isomer (determined by spectroscopic analysis). Controlled bromination of the resulting oxime (2) gave either a monobromo oxime, a dibromo oxime, or a spiroisoxazoline (Boehlow & Spilling, 1995). While the oxidative cyclization of the oxime gave indirect evidence for the *E* geometry (Boehlow & Spilling, 1995; for other examples, see Kacan, Koyuncu & McKillop, 1993; Forrester, Thomson & Woo, 1978*a,b*; Noda, Niwa

& Yamamura, 1981), we were unable to elucidate the geometry *via* spectroscopic methods. Herein, we report the structure and stereochemistry of ethyl 3-(3-bromo-4-hydroxyphenyl)-2*E*-(hydroxyimino)propanoate, (3).



The X-ray crystal structure (Fig. 1) clearly shows the *trans* arrangement of the carboxylate C atom and the oxime hydroxy group. The structures of three other α -oximino carboxylates have been reported (Bosman, Beurskens, Smits, Plate & Ottenhajm, 1986; Sliva, Simonov, Lampeka, Dvorkin & Mazus, 1989; Nakada *et al.*, 1981), and in all cases the oxime geometry was found to be *E*. In the crystal structure, two molecules form a head-to-tail hydrogen-bonded cyclic dimer, with the hydrogen bonds between the phenol H atom of one molecule and the carboxylate O atom of the other (Fig. 2). The O—H hydrogen-bond distance is 1.913 Å, with an O—H—O angle of 157.6°. The phenyl rings within the dimer are stacked with a distance of 5.659 Å between the ring planes. The dimers are hydrogen bonded *via* the oximes to form a repeating chain. The intermolecular N···H' hydrogen-bond distance is 2.261 Å with an N···N' distance of 2.836 Å.

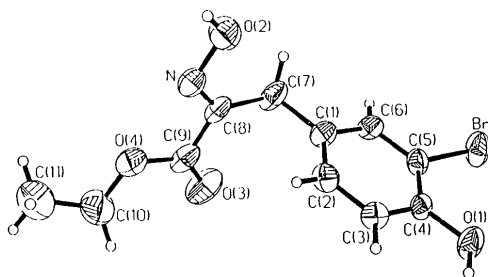


Fig. 1. The molecular structure of the oxime shown with 25% probability ellipsoids.

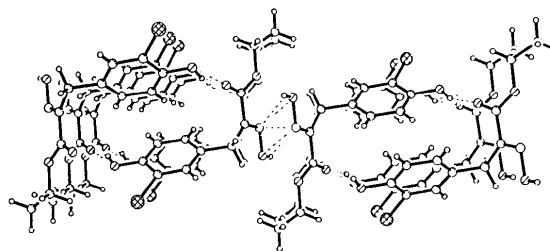


Fig. 2. The hydrogen-bonded chain of repeating head-to-tail hydrogen-bonded dimers, also showing the layered π -stacking arrangement.

Experimental

The oxime (2) was treated with 1 equivalent of *N*-bromoacetamide (NBA) in thf at 195 K to give the monobromotyrosine oxime derivative (3) in a 60% yield. Recrystallization from toluene at 273 K gave crystals suitable for X-ray diffraction.

Crystal data

$\text{C}_{11}\text{H}_{12}\text{BrNO}_4$
 $M_r = 302.13$
 Monoclinic
 $P2_1/n$
 $a = 9.715 (2) \text{ \AA}$
 $b = 5.659 (2) \text{ \AA}$
 $c = 22.763 (5) \text{ \AA}$
 $\beta = 100.10 (1)^\circ$
 $V = 1232.1 (6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.629 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 33 reflections
 $\theta = 5.0\text{--}14.6^\circ$
 $\mu = 3.339 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
 Rectangular
 $0.30 \times 0.20 \times 0.10 \text{ mm}$
 Colorless

Data collection

Siemens R3 diffractometer
 $2\theta/\omega$ scans
 Absorption correction:
 ψ scan (XEMP in
 SHELXTL-Plus; Sheldrick,
 1994)
 $T_{\min} = 0.542$, $T_{\max} =$
 0.685
 4743 measured reflections
 2855 independent reflections

1373 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.1508$
 $\theta_{\max} = 27.56^\circ$
 $h = -12 \rightarrow 12$
 $k = -2 \rightarrow 7$
 $l = -29 \rightarrow 29$
 3 standard reflections
 monitored every 100
 reflections
 intensity decay: 13%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0613$
 $wR(F^2) = 0.0920$
 $S = 1.114$
 2855 reflections
 162 parameters
 H atoms riding except
 H(O) which were refined
 isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.402 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.423 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Br	0.12507 (7)	0.09735 (14)	0.22300 (3)	0.0535 (2)
O(1)	0.0517 (4)	0.4842 (8)	0.3010 (2)	0.0503 (14)
O(2)	-0.3398 (4)	0.8589 (8)	0.0114 (2)	0.056 (2)
O(3)	-0.5606 (6)	0.3775 (10)	0.1275 (2)	0.077 (2)
O(4)	-0.6736 (5)	0.6782 (8)	0.0764 (2)	0.0519 (13)
N	-0.4553 (5)	0.8022 (9)	0.0366 (2)	0.0406 (13)
C(1)	-0.2189 (6)	0.4748 (11)	0.1373 (3)	0.037 (2)
C(2)	-0.2284 (6)	0.6501 (10)	0.1785 (3)	0.038 (2)
C(3)	-0.1408 (5)	0.6569 (10)	0.2332 (3)	0.034 (2)
C(4)	-0.0373 (6)	0.4903 (10)	0.2470 (3)	0.0306 (14)
C(5)	-0.0235 (5)	0.3150 (11)	0.2060 (3)	0.035 (2)
C(6)	-0.1133 (6)	0.3053 (11)	0.1517 (3)	0.036 (2)
C(7)	-0.3142 (6)	0.4515 (12)	0.0774 (3)	0.052 (2)
C(8)	-0.4383 (6)	0.6113 (13)	0.0677 (2)	0.041 (2)
C(9)	-0.5631 (7)	0.5409 (12)	0.0949 (3)	0.047 (2)
C(10)	-0.7993 (7)	0.6248 (16)	0.1004 (3)	0.071 (3)
C(11)	-0.9136 (8)	0.7703 (18)	0.0678 (4)	0.099 (4)

Table 2. Selected geometric parameters (Å, °)

Br—C(5)	1.885 (6)	C(1)—C(7)	1.513 (7)
O(1)—C(4)	1.375 (6)	C(2)—C(3)	1.381 (7)
O(2)—N	1.384 (6)	C(3)—C(4)	1.374 (7)
O(3)—C(9)	1.184 (7)	C(4)—C(5)	1.384 (7)
O(4)—C(9)	1.332 (7)	C(5)—C(6)	1.383 (7)
O(4)—C(10)	1.454 (7)	C(7)—C(8)	1.492 (8)
N—C(8)	1.286 (7)	C(8)—C(9)	1.509 (9)
C(1)—C(2)	1.379 (7)	C(10)—C(11)	1.474 (9)
C(1)—C(6)	1.401 (7)		
C(9)—O(4)—C(10)	116.3 (6)	C(6)—C(5)—Br	119.9 (5)
C(8)—N—O(2)	112.8 (5)	C(4)—C(5)—Br	119.4 (4)
C(2)—C(1)—C(6)	117.8 (5)	C(5)—C(6)—C(1)	120.2 (6)
C(2)—C(1)—C(7)	124.9 (6)	C(8)—C(7)—C(1)	115.5 (5)
C(6)—C(1)—C(7)	117.3 (6)	N—C(8)—C(7)	127.8 (6)
C(1)—C(2)—C(3)	122.0 (6)	N—C(8)—C(9)	114.4 (6)
C(4)—C(3)—C(2)	119.8 (6)	C(7)—C(8)—C(9)	117.8 (6)
C(3)—C(4)—O(1)	122.8 (5)	O(3)—C(9)—O(4)	125.6 (7)
C(3)—C(4)—C(5)	119.5 (5)	O(3)—C(9)—C(8)	122.3 (7)
O(1)—C(4)—C(5)	117.7 (5)	O(4)—C(9)—C(8)	112.1 (6)
C(6)—C(5)—C(4)	120.6 (5)	O(4)—C(10)—C(11)	107.7 (6)

The structure was solved by Patterson methods and refined successfully in the monoclinic space group *P*₂₁/*n*. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. Hydroxy H atoms were refined isotropically whereas the remaining H atoms were refined using an appropriate riding model.

Data collection: *P3/PC Diffractometer Program* (Siemens, 1989a). Cell refinement: *P3/PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1989b). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,3-Diphenylpropan-1-one

NENAD JUDAŠ, BRANKO KAITNER* AND ERNEST MEŠTROVIĆ

Chemistry Department, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, ul. Kralja Zvonimira 8, 41000 Zagreb, Croatia

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Abstract

The stereochemistry of the title compound, C₁₅H₁₄O, is similar to that of the analogous compounds 2-phenylacetophenone and substituted and non-substituted phenyl benzoate, although the middle part of the title molecule contains an additional methylene group. The phenyl rings are twisted with respect to both each