

- Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kato, M., Takenaka, A. & Sasada, Y. (1979). *Bull. Chem. Soc. Jpn.* **52**, 49–51.
- Louis, T., Low, J. N. & Tollin, P. (1982). *Cryst. Struct. Commun.* **11**, 1059–1064.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Wallace, P. M., MacMaster, J. F., Smith, V. F., Kerr, D. E., Senter, P. D. & Cosand, W. L. (1994). *Cancer Res.* **54**, 2719–2723.

Acta Cryst. (1995). **C51**, 2698–2700

(Z)-2,3-Bis(3,4-dimethoxyphenyl)propenoic Acid

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(Received 31 January 1995; accepted 5 July 1995)

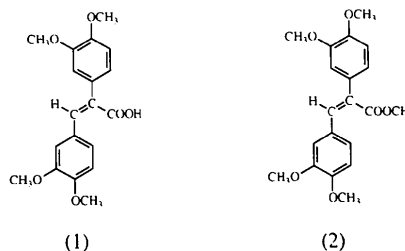
Abstract

The crystal structure determination demonstrates unambiguously that the title compound, C₁₉H₂₀O₆, has the Z configuration. The compound was synthesized starting from 2,3-bis(3,4-dimethoxyphenyl)-2-hydroxypropanoic acid, which was in turn obtained by an alkaline treatment of *trans*-1,3-bis(3,4-dimethoxyphenyl)-2,3-epoxy-1-propanone. ¹H NMR data for the title compound and its methyl ester are reported.

Comment

α-Arylcinnamic acids are of interest as intermediates in the syntheses of stilbenes. Gierer, Lenic, Norén & Szabo-Lin (1974) prepared a series of lignin-related stilbenes using α-arylcinnamic acids as starting materials. Such compounds (and their esters) can also be used as starting materials for the preparation of α-arylcinnamyl alcohols. Certain compounds of this latter type are intermediates in the acid-catalysed reactions of lignin models of the 1,2-diaryl-1,3-propanediol type (Li & Lundquist,

1995). The X-ray work presented in this study establishes the structure and stereochemistry of such an α-arylcinnamic acid, namely, (Z)-2,3-bis(3,4-dimethoxyphenyl)propenoic acid, (1). Since the synthesis of α-arylcinnamyl alcohols from α-arylcinnamic acids usually proceeds *via* the ester derivatives, we also prepared the methyl ester of (1), *i.e.* (2), and examined it by X-ray crystallographic methods. Attempts to obtain good crystals of (2) failed (the crystals often suddenly cracked, a possible explanation being internal strain). However, a structure analysis was performed and it could be concluded that (2) had the expected Z configuration.



The title acid (1), contaminated with minor amounts of the *E* form, was obtained by heating 2,3-bis(3,4-dimethoxyphenyl)-2-hydroxypropanoic acid with acetic

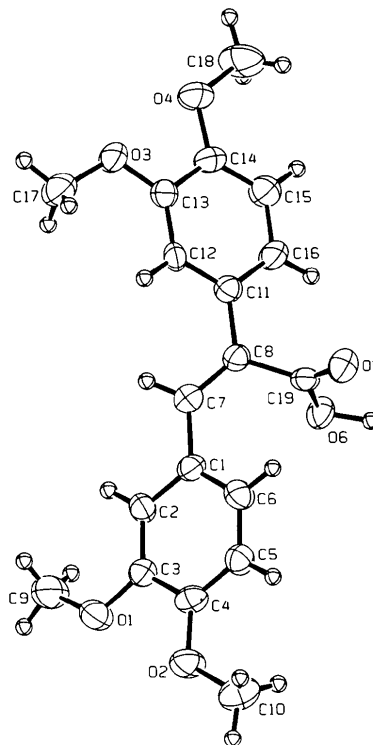


Fig. 1. A perspective drawing (*ORTEP*II; Johnson, 1976) of compound (1), with displacement ellipsoids at the 50% level, showing the numbering of the non-H atoms. H atoms are shown as small spheres of arbitrary radii.

anhydride/sodium acetate. Recrystallization from acetic acid gave pure (1) (m.p. 443–444 K). The propanoic acid derivative used as starting material was obtained by an alkali-catalyzed conversion of *trans*-1,3-bis(3,4-dimethoxyphenyl)-2,3-epoxy-1-propanone. The methyl ester, (2), was prepared from (1) and methyl iodide.

A perspective view of (1) is shown in Fig. 1. This crystal structure determination demonstrates unambiguously that acid (1) has the *Z* configuration.

Crystals of (1) are stabilized by hydrogen bonds. It is notable that the benzylic C(8) atom in (1) is twisted by 0.114(6) Å out of the plane of the C(11)–C(16) aromatic ring [atom C(7) is located near the C(1)–C(6) plane, with a deviation of 0.023(8) Å]. The atoms of the carboxyl group are coplanar within 1σ. The plane thus defined forms an angle of 107.7(5)° with the plane defined by atoms C(1), C(7), C(8), C(11) and C(19). The angle between the aromatic ring planes is 60.1(5)° in compound (1).

Experimental

Compound (1) was synthesized starting from 2,3-bis(3,4-dimethoxyphenyl)-2-hydroxypropanoic acid. This compound was prepared from *trans*-1,3-bis(3,4-dimethoxyphenyl)-2,3-epoxy-1-propanone (Stomberg, Li & Lundquist, 1994) according to a synthetic procedure used for the preparation of substituted mandelic acids (Pandit & Gadre, 1988). A product melting at 434–435 K was obtained (yield 85%). ¹H NMR spectrum (400 MHz, CDCl₃, 293 K, TMS) of 2,3-bis(3,4-dimethoxyphenyl)-2-hydroxypropanoic acid: δ 3.14 (1H, *d*, *J* = 13.6 Hz, CH₂), 3.59 (1H, *d*, *J* = 13.6 Hz, CH₂), 3.76 (3H, *s*, OCH₃), 3.84 (3H, *s*, OCH₃), 3.886 (3H, *s*, OCH₃), 3.893 (3H, *s*, OCH₃), 6.5–7.3 p.p.m. (6H, *m*, H-Ar). For the preparation of (*Z*)-2,3-bis(3,4-dimethoxyphenyl)propenoic acid, (1), [cf. the method for the preparation of α-arylcinnamic acids described by Gadre & Marathe (1988)], 2,3-bis(3,4-dimethoxyphenyl)-2-hydroxypropanoic acid (3.62 g, 10 mmol) was refluxed with acetic anhydride (100 ml) and fused sodium acetate (2.51 g, 30 mmol) for 1 h. Water (40 ml) was added to the hot reaction mixture, which was then set aside overnight at room temperature. On addition of water (300 ml) a precipitate formed. After 2 h the precipitate was filtered off and dried. The product (3.28 g) consisted primarily of the target molecule, contaminated with the *E* isomer (thin-layer chromatography, ¹H NMR). A reference sample of the *E* isomer was prepared according to methods described in the literature (Battersby & Greenock, 1961; Russell & Hunziker, 1969). Two recrystallizations from acetic acid gave 1.98 g of pure *Z* acid (m.p. 443–444 K; yield 58%). ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 293 K, TMS): δ 3.76 (3H, *s*, OCH₃), 3.78 (6H, *s*, OCH₃), 3.82 (3H, *s*, OCH₃), 6.9–7.2 [7H, *m*, H-Ar and vinyl proton (δ 6.94)], 13.3 p.p.m. [1H, *s* (broad), COOH].

The methyl ester, (2), of (*Z*)-2,3-bis(3,4-dimethoxyphenyl)propenoic acid was prepared using a procedure analogous to that reported for the preparation of methyl (2,6-dimethoxyphenoxy)acetate (Lundquist, Stomberg & von Unge, 1987). The crude product was freed from tetrabutylammonium iodide by leaching with hot water. Crystallization from ethanol gave a product melting at 421 K (yield 86%). ¹H NMR spectrum

(400 MHz, CDCl₃, 293 K, TMS): δ 3.82 (3H, *s*, OCH₃), 3.89 (3H, *s*, OCH₃), 3.902 (3H, *s*, OCH₃), 3.904 (3H, *s*, OCH₃), 3.92 (3H, *s*, OCH₃), 6.8–7.0 p.p.m. (7H, *m*, H-Ar and vinyl proton).

Crystal data

C₁₉H₂₀O₆
 $M_r = 344.36$
 Orthorhombic
*Pca*2₁
 $a = 8.884(3)$ Å
 $b = 26.179(2)$ Å
 $c = 7.286(2)$ Å
 $V = 1694.6(8)$ Å³
 $Z = 4$
 $D_x = 1.350$ Mg m^{−3}

Mo *K*α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 11.3$ – 19.9°
 $\mu = 0.094$ mm^{−1}
 $T = 295$ K
 Rod
 0.40 × 0.12 × 0.09 mm
 Colourless

Data collection

Rigaku AFC-6R diffractometer
 ω scans
 Absorption correction: none
 2945 measured reflections
 1777 independent reflections
 1701 observed reflections
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 10$
 $k = -26 \rightarrow 31$
 $l = -7 \rightarrow 8$
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.5%

Refinement

Refinement on F
 $R = 0.034$
 $wR = 0.041$
 $S = 1.16$
 887 reflections
 229 parameters
 H-atom parameters not refined, except for H(O6)
 $w = 1/[\sigma^2(F_o) + 0.05(F_o)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.02$
 $\Delta\rho_{\text{max}} = 0.14$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.15$ e Å^{−3}
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
C(1)	0.3675 (6)	0.3176 (2)	0.2183	2.9 (2)
C(2)	0.2178 (5)	0.3337 (2)	0.230 (1)	3.0 (2)
C(3)	0.1821 (5)	0.3823 (2)	0.289 (1)	3.0 (2)
C(4)	0.2949 (6)	0.4169 (2)	0.335 (1)	3.2 (3)
C(5)	0.4446 (6)	0.4016 (2)	0.319 (1)	3.4 (3)
C(6)	0.4784 (5)	0.3524 (2)	0.262 (1)	3.5 (3)
C(7)	0.3989 (6)	0.2654 (2)	0.154 (1)	3.3 (3)
C(8)	0.5126 (6)	0.2346 (2)	0.200 (1)	2.8 (2)
C(9)	−0.0803 (6)	0.3662 (2)	0.280 (1)	5.2 (3)
C(10)	0.3603 (7)	0.4991 (2)	0.452 (1)	5.2 (3)
C(11)	0.5390 (6)	0.1835 (2)	0.117 (1)	3.0 (2)
C(12)	0.4870 (6)	0.1710 (2)	−0.056 (1)	2.8 (2)
C(13)	0.5004 (6)	0.1225 (2)	−0.127 (1)	3.0 (3)
C(14)	0.5741 (6)	0.0845 (2)	−0.024 (1)	3.3 (3)
C(15)	0.6319 (7)	0.0969 (2)	0.146 (1)	3.9 (3)
C(16)	0.6141 (6)	0.1459 (2)	0.215 (1)	3.9 (3)
C(17)	0.3515 (7)	0.1386 (2)	−0.392 (1)	4.6 (3)
C(18)	0.6597 (8)	−0.0016 (2)	−0.007 (1)	5.9 (4)
C(19)	0.6268 (7)	0.2497 (2)	0.342 (1)	2.7 (2)
O(1)	0.0380 (4)	0.4013 (1)	0.302 (1)	4.2 (2)
O(2)	0.2475 (5)	0.4638 (1)	0.392 (1)	4.1 (2)
O(3)	0.4521 (4)	0.1068 (1)	−0.295 (1)	4.5 (2)

O(4)	0.5840 (4)	0.0378 (1)	−0.107 (1)	4.2 (2)
O(5)	0.7566 (5)	0.2596 (1)	0.308 (1)	3.5 (2)
O(6)	0.5722 (4)	0.2487 (1)	0.511 (1)	3.5 (2)

Table 2. Selected geometric parameters (Å, °)

C(1)—C(2)	1.398 (7)	C(10)—O(2)	1.432 (7)
C(1)—C(6)	1.379 (7)	C(11)—C(12)	1.380 (8)
C(1)—C(7)	1.471 (7)	C(11)—C(16)	1.389 (7)
C(2)—C(3)	1.380 (7)	C(12)—C(13)	1.376 (6)
C(3)—C(4)	1.390 (6)	C(13)—C(14)	1.409 (7)
C(3)—O(1)	1.377 (6)	C(13)—O(3)	1.360 (7)
C(4)—C(5)	1.394 (7)	C(14)—C(15)	1.380 (8)
C(4)—O(2)	1.362 (6)	C(14)—O(4)	1.368 (6)
C(5)—C(6)	1.385 (7)	C(15)—C(16)	1.384 (7)
C(7)—C(8)	1.337 (7)	C(17)—O(3)	1.412 (7)
C(8)—C(11)	1.486 (7)	C(18)—O(4)	1.434 (7)
C(8)—C(19)	1.505 (8)	C(19)—O(5)	1.209 (6)
C(9)—O(1)	1.405 (7)	C(19)—O(6)	1.321 (6)
C(1)—C(7)—C(8)	128.6 (5)	C(8)—C(19)—O(6)	113.0 (5)
C(2)—C(3)—O(1)	124.7 (4)	O(5)—C(19)—O(6)	123.2 (5)
C(5)—C(4)—O(2)	125.3 (5)	C(3)—O(1)—C(9)	116.8 (4)
C(12)—C(13)—O(3)	126.1 (5)	C(4)—O(2)—C(10)	117.4 (5)
C(15)—C(14)—O(4)	125.8 (5)	C(13)—O(3)—C(17)	118.3 (4)
C(8)—C(19)—O(5)	123.8 (5)	C(14)—O(4)—C(18)	116.5 (5)
C(1)—C(7)—C(8)—C(11)	−175.9 (5)		
C(1)—C(7)—C(8)—C(19)	3.6 (9)		
C(7)—C(8)—C(19)—O(5)	−110.5 (6)		

D—H...A	D...A	D—H...A
O(6)—H(O6)...O(5 ⁱ)	2.659 (5)	153 (7)

Symmetry code: (i) $\frac{2}{3} - x, y, \frac{1}{2} + z$.

The collection of the data was extended to include reflections of the type $h\bar{k}l$. A small number of reflections were affected by a minor contribution from a satellite crystal (usually this was not the case for both a reflection of the type hkl and the corresponding reflection of the type $h\bar{k}l$). The affected reflections were omitted from the data set and average F values were calculated and used in the structure analysis.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1985). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Battersby, A. R. & Greenock, I. A. (1961). *J. Chem. Soc.* pp. 2592–2593.
- Gadre, S. Y. & Marathe, K. G. (1988). *Synth. Commun.* **18**, 1015–1027.
- Gierer, J., Lenic, J., Norén, I. & Szabo-Lin, I. (1974). *Acta Chem. Scand. Ser. B*, **28**, 717–729.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Li, S. & Lundquist, K. (1995). *Proceedings of the 8th International Symposium on Wood and Pulp Chemistry*, June 6–9, Helsinki, Finland, Vol. 1, pp. 163–167, and unpublished data.
- Lundquist, K., Stomberg, R. & von Unge, S. (1987). *Acta Chem. Scand. Ser. B*, **41**, 499–510.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pandit, S. B. & Gadre, S. Y. (1988). *Synth. Commun.* **18**, 157–166.

Russell, J. H. & Hunziker, H. (1969). *Tetrahedron Lett.* pp. 4035–4036.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Stomberg, R., Li, S. & Lundquist, K. (1994). *J. Chem. Crystallogr.* **24**, 407–413.

Acta Cryst. (1995). **C51**, 2700–2702

2-[2-(3,4-Dichlorophenyl)vinyl]benzo-[d]thiazole

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(Received 1 December 1994; accepted 26 June 1995)

Abstract

The title compound, C₁₅H₉Cl₂NS, was synthesized by the condensation of 1-(3,4-dichlorophenyl)-4-methyl-1-penten-3-one and 2-aminothiophenol. The title compound is essentially planar in the solid state. The C=C double bond has the *E* configuration.

Comment

The synthesis of the title compound, (III), was unexpected and arose presumably by initial formation of an anil between 1-(3,4-dichlorophenyl)-4-methyl-1-penten-3-one, (I), and 2-aminothiophenol, (II), followed by attack on the carbimino C atom by the S atom leading to the extrusion of the isopropyl group and ring closure forming a benzothiazole. Alternatively, attack by the S atom on the carbonyl C atom of (I) could lead to an intermediate, the amino group of which subsequently forms a bond with this C atom, leading to ring closure and the elimination of the isopropyl group.