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4-Hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.111
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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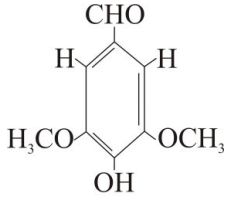
Molecules of syringaldehyde, $C_9H_{10}O_4$, are connected by intermolecular O—H···O [H···O = 2.05 Å and O···O = 2.713 (2) Å] hydrogen bonds between the 4-hydroxy and 1-aldehyde functions into infinite linear chains. The 4-hydroxy H atoms also participate in an intramolecular O—H···O [H···O = 2.22 Å and O···O = 2.662 (2) Å] interaction with a neighbouring methoxy O atom.

Comment

In the course of our spectroscopic and structural studies of some 'push–pull' substituted aldehydes having non-linear optical, photorefractive and electro-optical properties (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987), the crystal structure of the title compound, syringaldehyde (I), has been determined.



(I)

The IR spectrum of (I) (KBr pellet) exhibits no characteristic sharp bands for ν(OH). A band of middle intensity appears at 3300 cm^{-1}. The very intense and highly symmetric ν(C═O) band of (I) is at 1670 cm^{-1}. Another prominent band is that at 1109 cm^{-1}, belonging to ν(C—O) of the methoxy groups. We compared this spectrum with that of vanillin (4-hydroxy-3-methoxybenzaldehyde), which can be used as a model system for an IR study of the influence of hydroxy and methoxy groups on the ν(C═O) band. The comparison shows that the spectra of (I) and vanillin are similar, but that of the former is more complicated. These circumstances motivated us to calculate the theoretical spectrum of (I) at *ab initio* RHF 6-31G* and DFT B3LYP 6-31G* levels. The resulting theoretical frequencies verified our assumption that a strong intermolecular hydrogen bond exists between the —OH and O═CH— groups of (I), in addition to an intramolecular hydrogen bond between the —OH and —OCH_3 functions. The IR spectrum of (I) in dilute chloroform solution (c = 10^{-1} *M*) shows two bands in the ν(C═O) region at 1688 and 1710 cm^{-1}. The first is assigned to a hydrogen-bonded ν(C═O) and the second to the free one. In the same solvent at a concentration of 10^{-3} *M*, the band at 1688 cm^{-1} practically disappears and that at 1710 cm^{-1} increases in intensity. The bands belonging to ν(O—H) appear at 3531 and 3524 cm^{-1} at this dilution and could be assigned to the two possible

different conformers where the OH group is connected to either of the two methoxy groups. Detailed vibrational and quantum-chemical investigations are in progress and will be published at a later date. The crystal structure of (I) confirms the presence of intermolecular O4—H4···O1^{i} hydrogen bonds that are complemented by C11—H11···O4^{ii} interactions (see Table 1 for symmetry codes). As indicated by IR analysis, the hydroxy atom H4 also participates in an intramolecular O4—H4···O5 contact (Table 1). Infinite chains of (I) extend in the directions [110] and [1$\bar{1}$0].

Experimental

Compound (I) was obtained commercially (Lancaster Synthesis GmbH) as a grey powder and was recrystallized four times, firstly from water–ethanol and then three times from 96% ethanol. The IR and Raman spectra of (I) were measured after each recrystallization and confirm the compound stability. Single prismatic and colourless crystals suitable for X-ray analysis were grown from ethanol at room temperature.

Crystal data

$C_9H_{10}O_4$
M_r = 182.17
Monoclinic, $P2_1/n$
a = 6.9076 (10) Å
b = 4.895 (3) Å
c = 25.213 (4) Å
β = 91.349 (7)°
V = 852.2 (6) Å^3
Z = 4
D_x = 1.420 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 reflections
θ = 8.2–12.4°
μ = 0.11 mm^{-1}
T = 293 (2) K
Prism, colourless
0.42 × 0.36 × 0.34 mm

Data collection

Siemens $P4$ four-circle diffractometer
ω scans
2332 measured reflections
1483 independent reflections
1252 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 25.0°
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 5$
$l = -29 \rightarrow 29$
3 standard reflections
every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.111
S = 1.04
1483 reflections
121 parameters
H-atoms parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.1548P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.122 (16)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1^{i}	0.82	2.05	2.7133 (19)	138
C11—H11···O4^{ii}	0.93	2.51	2.978 (2)	112
O4—H4···O5	0.82	2.22	2.6618 (15)	114

Symmetry codes: (i) $x-1, y-1, z$; (ii) $1+x, 1+y, z$.

H atoms were refined with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(O), 1.2 U_{eq}(C) or 1.5 U_{eq}(C$_{methyl}$)] using a riding model, with O—H = 0.82 Å, aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å. The methyl groups were allowed to rotate about their local threefold axes.

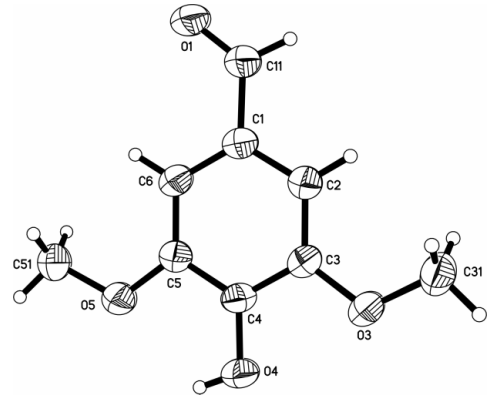


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

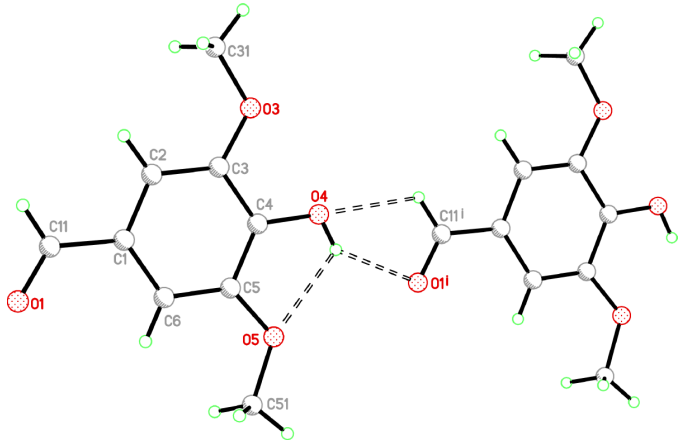


Figure 2
Linkage of the molecules of (I) into infinite chains through intermolecular O—H···O hydrogen bonds. [Symmetry code: (i) $x-1, y-1, z$.]

Data collection: *R3m/V User's Guide* (Siemens, 1989); cell refinement: *R3m/V User's Guide*; data reduction: *XDISK* in *R3m/V User's Guide*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

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References

Chemla, D. & Zyss, J. (1987). Editors. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, pp. 23–187. New York: Academic Press.
Nalwa, H. S., Watanabe, T. & Miyata, S. (1997). *Nonlinear Optics of Organic Molecules and Polymers*, edited by H. S. Nalwa and S. Miyata, pp. 89–329. Boca Raton: CRC Press.
Sheldrick, G. M. (1995). *SHELXTL-Plus.* Release 5.03 for Siemens *R*3 crystallographic research system. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1989). *R3m/V User's Guide.* Version 3.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wolff, J. J. & Wortmann, R. (1999). *Adv. Phys. Org. Chem.* **32**, 121–217.