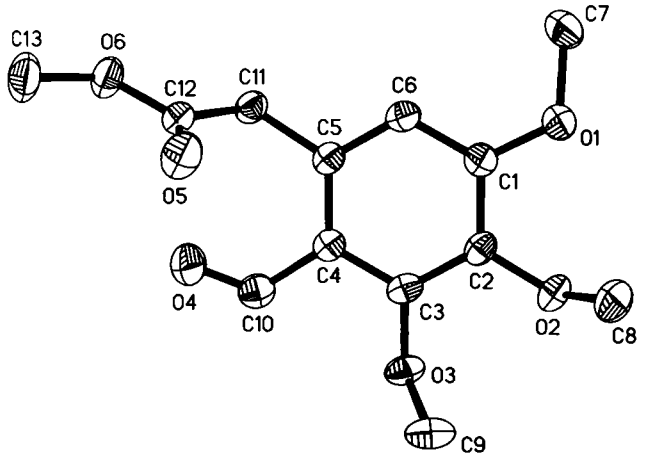
Z. Kristallogr. NCS 221 (2006) 497-498 / DOI 10.1524/ncrs.2006.0171

Crystal structure of methyl 2-(2-formyl-3,4,5-trimethoxyphenyl)acetate, $C_{13}H_{16}O_6$

G. S. Khan[I], N. H. Rama*,[I], G. Qadeer[I], A. Noor[II] and R. Kempe[II]

[I] Quaid-i-Azam University, Department of Chemistry, 45320 Islamabad, Pakistan
[II] Universität Bayreuth, Lehrstuhl für Anorganische Chemie II, 95440 Bayreuth, Germany

Received September 20, 2006, accepted and available on-line November 20, 2006; CCDC no. 1267/1897



Abstract

$C_{13}H_{16}O_6$, triclinic, $P\bar{1}$ (no. 2), a = 7.343(2) Å, b = 8.972(2) Å, c = 10.152(2) Å, α = 81.12(2)°, β = 77.997(2)°, γ = 80.22(2)°, V = 639.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.081, $wR_{ref}(F^2)$ = 0.239, T = 191 K.

Source of material

Phosphorus oxychloride (5.3 g, 0.034 mol) was added drop wise to a stirred solution of methyl 3,4,5-trimethoxyphenylacetate (7 g, 0.029 mol) in freshly distilled *N,N*-dimethylformamide (30 ml) at 550 °C. The solution was then heated at 100 °C for 10 minutes and stirred overnight. The reaction mixture was poured into aqueous sodium acetate (10 %, 300 ml) with stirring. The resultant precipitate was recrystallized from ethyl acetate to yield methyl 2-formyl-3,4,5-trimethoxyphenylacetate (4.5 g, 0.0168 mol) as colorless crystals suitable for the X-ray single-crystal structure analysis.

Experimental details

The large R values are caused by the slightly poor quality of the crystals. Solvent molecules were not found in the structure. Only the H1atom (at C10) was refined due its importance in the hydrogen bonding, while the other H atoms were added geometrically.

Discussion

The reported compound known as methyl 2-formyl-3,4,5-trimethoxyphenyl-acetate is the intermediate for the synthesis of naturally occurring biological active isocoumarins and 3,4-dihydroisocoumarins. The most important naturally occurring isocoumarins synthesized by the title compound is (+)-kigelin [1]. In the title crystal structure, the bonds lengths within phenyl ring lie between 1.383(3) Å and 1.410(2) Å which highlights the aromatic character. The valence angle C2–C3–C4 (121.7(2)°) is larger than the standard value of 120°. The opening of this angle is due to the presence of the two methoxy and one formyl groups on C2, C3 and C4, respectively, which involves a decrease of the ring angles of C1 (119.5(2)°) and C4 (118.5(2)°). The C10—O4 (1.202(3) Å) and C12—O6 (1.336(2) Å) bond distances are compatible with respective distances in related structures [2-4] and smaller than those usually observed in carboxylic acids (1.365 Å). The structure is influenced by intra- and intermolecular hydrogen bonding. The formyl H atom forms an intramolecular bond to the corresponding methoxy O atoms, i.e. C–H···O (d(H1···O3) = 2.279 Å. The crystal structure is stabilized by intermolecular C–H···O hydrogen bonds, whereas the formyl H atom of a molecule A interacts with the O atom of the ester group of the neighboring molecule B (d(H10A···O5B) = 2.689 Å) and the H atom of the ester group of the molecule B interacts with the O atom of the formyl group of the molecule A (d(H13B···O4A) = 2.628 Å). Simultaneously, the ester group present on molecule A interacts with the formyl group of another neighboring molecule C in a quite similar fashion.

* Correspondence author (e-mail: nasim_hasan_rama@hotmail.com)

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.46 × 0.45 × 0.70 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	1.11 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{max}$:	51.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8287, 2372
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2175
$N(param)_{refined}$:	176
Programs:	SIR97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(17)	2*i*	0.1349	0.1774	0.3921	0.033
H(19A)	2*i*	0.2183	0.2775	0.0415	0.078
H(19B)	2*i*	0.0967	0.3021	0.1888	0.078
H(19C)	2*i*	0.2082	0.1374	0.1601	0.078
H(10A)	2*i*	0.7643	0.5019	0.1067	0.064
H(10B)	2*i*	0.6258	0.5504	0.2420	0.064
H(10C)	2*i*	0.5468	0.4821	0.1319	0.064
H(8A)	2*i*	0.9170	0.4049	0.5163	0.061
H(8B)	2*i*	0.6969	0.4660	0.5516	0.061
H(8C)	2*i*	0.7980	0.4531	0.3973	0.061
H(16A)	2*i*	0.1863	−0.0119	0.6949	0.035
H(16B)	2*i*	0.0346	0.0602	0.6019	0.035
H(18A)	2*i*	−0.2737	0.1174	1.0243	0.070
H(18B)	2*i*	−0.2810	0.2719	0.9218	0.070
H(18C)	2*i*	−0.1155	0.2251	1.0074	0.070
H(1)	2*i*	0.615(4)	0.160(3)	0.717(3)	0.048(7)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.3863(2)	0.2513(2)	0.3108(2)	0.0291(9)	0.0246(9)	0.0286(9)	−0.0037(7)	−0.0043(7)	−0.0054(7)
C(2)	2*i*	0.5552(2)	0.2767(2)	0.3423(2)	0.0240(9)	0.0226(9)	0.0299(9)	−0.0032(7)	0.0017(7)	−0.0051(7)
C(3)	2*i*	0.5850(2)	0.2385(2)	0.4743(2)	0.0208(9)	0.0214(9)	0.035(1)	−0.0015(7)	−0.0035(7)	−0.0061(7)
C(4)	2*i*	0.4496(2)	0.1764(2)	0.5780(2)	0.0252(9)	0.0225(9)	0.0293(9)	−0.0017(7)	−0.0030(7)	−0.0049(7)
C(5)	2*i*	0.2793(2)	0.1545(2)	0.5455(2)	0.0246(9)	0.0223(9)	0.0292(9)	−0.0029(6)	−0.0006(7)	−0.0065(6)
C(6)	2*i*	0.2501(2)	0.1921(2)	0.4134(2)	0.0237(8)	0.0279(9)	0.0312(9)	−0.0048(7)	−0.0040(7)	−0.0063(7)
C(7)	2*i*	0.2112(4)	0.2474(3)	0.1393(2)	0.061(1)	0.069(2)	0.037(1)	−0.033(1)	−0.022(1)	0.007(1)
C(8)	2*i*	0.6551(3)	0.4771(2)	0.1756(2)	0.052(1)	0.036(1)	0.041(1)	−0.0184(9)	−0.0075(9)	0.0050(8)
C(9)	2*i*	0.7947(3)	0.4065(2)	0.4915(2)	0.033(1)	0.033(1)	0.062(1)	−0.0061(8)	−0.0170(9)	−0.0108(9)
C(10)	2*i*	0.4929(3)	0.1368(2)	0.7152(2)	0.032(1)	0.035(1)	0.039(1)	−0.0045(8)	−0.0077(8)	−0.0041(8)
C(11)	2*i*	0.1284(2)	0.0850(2)	0.6495(2)	0.0286(9)	0.0290(9)	0.031(1)	−0.0088(7)	−0.0009(7)	−0.0058(7)
C(12)	2*i*	0.0271(2)	0.1851(2)	0.7570(2)	0.0233(8)	0.032(1)	0.0269(9)	−0.0061(7)	−0.0026(6)	−0.0028(7)
C(13)	2*i*	−0.1978(3)	0.1864(3)	0.9601(2)	0.046(1)	0.057(1)	0.033(1)	−0.009(1)	0.0096(9)	−0.0120(9)
O(1)	2*i*	0.3715(2)	0.2841(2)	0.1790(1)	0.0420(8)	0.0437(9)	0.0286(7)	−0.0165(6)	−0.0089(6)	−0.0007(6)
O(2)	2*i*	0.6970(2)	0.3261(2)	0.2432(1)	0.0299(7)	0.0343(8)	0.0331(8)	−0.0101(6)	0.0030(6)	−0.0009(5)
O(3)	2*i*	0.7537(2)	0.2537(2)	0.5051(1)	0.0230(7)	0.0300(8)	0.0450(8)	−0.0056(5)	−0.0111(5)	0.0002(6)
O(4)	2*i*	0.3872(2)	0.0923(2)	0.8152(2)	0.0504(9)	0.059(1)	0.0329(8)	−0.0136(8)	−0.0077(7)	0.0047(7)
O(5)	2*i*	0.0360(2)	0.3169(2)	0.7556(2)	0.0461(9)	0.0327(8)	0.0442(9)	−0.0110(6)	0.0057(6)	−0.0112(6)
O(6)	2*i*	−0.0850(2)	0.1051(2)	0.8525(1)	0.0372(8)	0.0380(8)	0.0315(7)	−0.0117(6)	0.0065(6)	−0.0056(6)

Acknowledgment. We thank the Higher Education Commission of Islamabad for financial support of this study.

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