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Crystal structure of 2-(2-propynyloxy)benzaldehyde, $C_{10}H_8O_2$

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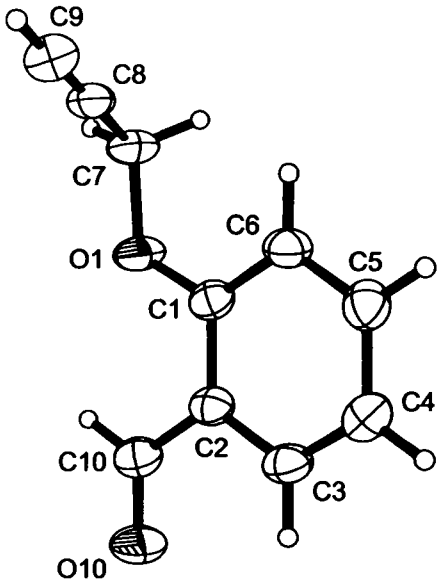

Abstract

$C_{10}H_8O_2$, triclinic, $P\bar{1}$ (no. 2), a = 4.3814(5) Å, b = 10.021(1) Å, c = 10.040(1) Å, α = 67.097(3)°, β = 87.762(3)°, γ = 80.576(4)°, V = 400.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.089, T = 200 K.

Source of material

2-(2-Propynyloxy)benzaldehyde was synthesized by the reaction of salicylaldehyde and propargyl bromide in the presence of potassium carbonate as a base in THF or acetone under reflux. After filtration and removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography with a mixture of petroleum ether/ethyl acetate (1:1, *v/v*) as eluent. The product was crystallized from petroleum ether/dichloromethane (3:1, *v/v*).

Experimental details

All hydrogen atoms were located from difference Fourier maps. In the refinement they were treated using appropriate riding models.

Discussion

Alkyne units in a molecule serve as rigid spacers between other fragments. The two perpendicular π bonds enable conjugation between these fragments and impart due to the *sp* hybridization of the carbon atoms high energy into these compounds. The π conjugation has attracted synthetic chemists already in the 1960s for the construction of conjugated systems by coupling of α,ω-polyacetylenes to annulenes [1]. The condensation of salicylaldehyde derivatives with a diamine results in the formation of the Schiff base salen ligand. The coordination chemistry of the class of tetradentate Schiff base ligands with transition metal atoms is well investigated. The formation of the Schiff base, however, is not restricted to salicylaldehyde derivatives. It proceeds as well with other aromatic aldehydes [2,3].

Previously 2-(2-propynyloxy)benzaldehyde has been used as a starting material in cycloaddition reactions [4]. We envisioned to use the title compound as starting material for the synthesis of some new Schiff bases. Further on, it finally can serve as starting material for the synthesis of polyacetylenes, namely the dimeric diyne 2-[6-(2-formylphenoxy)-2,4-hexadiynyloxy]benzaldehyde [5]. The analysis of the crystal structure reveals that the distances in the aromatic ring are not completely uniform. The longest bond (140 pm) was found between the carbon atoms carrying the heterosubstituents (C1 and C2). The shortest bonds are the next but one bonds on both sides (C3–C4 and C5–C6). This pattern was also found in the crystal structure of the homocoupling product, the diyne [5].

Table 1. Data collection and handling.

Crystal:	colorless polyhedron, size 0.08 × 0.18 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2364, 1749
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 968
$N(param)_{refined}$:	109
Program:	SHELXTL [6]

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

Atom	Site	x	y	z	U_{iso}
H(3)	2*i*	0.2476	0.9519	0.4645	0.043
H(4)	2*i*	0.5393	1.0924	0.2803	0.046
H(5)	2*i*	0.7460	1.0014	0.1082	0.047
H(6)	2*i*	0.6511	0.7772	0.1156	0.043
H(7A)	2*i*	0.3970	0.4379	0.2328	0.046
H(7B)	2*i*	0.6495	0.5453	0.1861	0.046
H(9)	2*i*	0.0225	0.7361	−0.1430	0.052
H(10)	2*i*	0.0228	0.6122	0.5143	0.046

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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*	0.3883(3)	0.7303(2)	0.2951(2)	0.0348(9)	0.031(1)	0.0270(9)	–0.0021(7)	–0.0029(7)	–0.0119(7)
O(1)	2*i*	0.3194(2)	0.5970(1)	0.3083(1)	0.0540(7)	0.0365(7)	0.0304(6)	–0.0093(5)	0.0099(5)	–0.0193(5)
C(2)	2*i*	0.2688(3)	0.7814(2)	0.4009(2)	0.0309(9)	0.035(1)	0.0247(8)	–0.0002(7)	–0.0037(7)	–0.0132(7)
C(3)	2*i*	0.3287(3)	0.9164(2)	0.3932(2)	0.036(1)	0.043(1)	0.0334(9)	0.0005(8)	–0.0038(8)	–0.0221(8)
C(4)	2*i*	0.5026(4)	0.9999(2)	0.2848(2)	0.042(1)	0.036(1)	0.041(1)	–0.0054(8)	–0.0043(8)	–0.0181(8)
C(5)	2*i*	0.6229(4)	0.9457(2)	0.1826(2)	0.040(1)	0.043(1)	0.0344(9)	–0.0121(8)	0.0003(7)	–0.0136(8)
C(6)	2*i*	0.5672(4)	0.8125(2)	0.1867(2)	0.038(1)	0.043(1)	0.0299(9)	–0.0054(8)	0.0037(7)	–0.0190(8)
C(7)	2*i*	0.4254(4)	0.5418(2)	0.1992(2)	0.049(1)	0.037(1)	0.0345(9)	–0.0034(8)	0.0072(8)	–0.0220(8)
C(8)	2*i*	0.2619(4)	0.6250(2)	0.0595(2)	0.041(1)	0.039(1)	0.0345(9)	–0.0103(8)	0.0103(8)	–0.0233(8)
C(9)	2*i*	0.1298(4)	0.6863(2)	–0.0523(2)	0.048(1)	0.049(1)	0.040(1)	–0.0089(9)	0.0022(9)	–0.0232(9)
C(10)	2*i*	0.0765(4)	0.6995(2)	0.5164(2)	0.044(1)	0.041(1)	0.0316(9)	–0.0048(8)	0.0001(8)	–0.0168(8)
O(10)	2*i*	–0.0195(2)	0.7353(1)	0.6150(1)	0.0588(8)	0.0550(9)	0.0333(7)	–0.0073(6)	0.0101(6)	–0.0248(6)

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