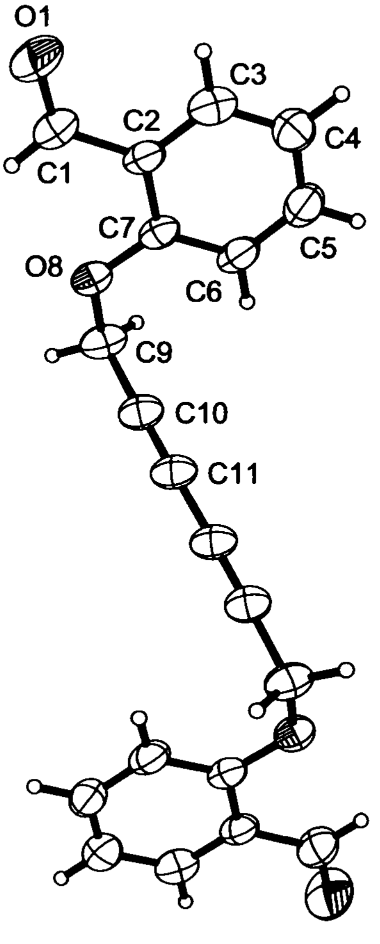
Z. Kristallogr. NCS **221** (2006) 339-340 / **DOI** 10.1524/ncrs.2006.0100

Crystal structure of 2-[6-(2-formylphenoxy)-2,4-hexadiynyloxy]-benzaldehyde, $C_{20}H_{14}O_4$

D. B. Werz[I], S. Balalaie*,[II], F. Rominger[III] and Z. Oloumi[II]

[I] ETH-Hönggerberg, Swiss Federal Institute of Technology, Laboratory for Organic Chemistry, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland
[II] K. N. Toosi University of Technology, Chemistry Department, P.O. Box 15875-4416, Tehran 15418, Iran
[III] Universität Heidelberg, Organisch-Chemisches Institut, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Received June 20, 2006, accepted and available on-line August 10, 2006; CCDC no. 1267/1819



Abstract

$C_{20}H_{14}O_4$, monoclinic, $P12_1/c1$ (no. 14), $a = 12.5632(6)$ Å, $b = 4.3769(2)$ Å, $c = 14.8059(8)$ Å, $\beta = 104.213(2)°$, $V = 789.2$ Å^3, $Z = 2$, $R_{gt}(F) = 0.053$, $wR_{ref}(F^2) = 0.145$, $T = 200$ K.

Source of material

2-[6-(2-Formylphenoxy)-2,4-hexadiynyloxy]benzaldehyde was synthesized according to two different methods: (a) Homocoupling of the acetylenic compound 2-(2-propynyloxy)benzaldehyde [1] with $Cu(OAc)_2$ with or without pyridine (Eglinton reaction), (b) Reaction of salicylaldehyde and 1,6-ditosyl-2,4-hexadiyne in the presence of potassium carbonate as a base in THF over 24 h. 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 products were crystallized from petroleum ether/dichloromethane (3:1, *v/v*; m.p. 146-147 °C). Analytical data are available in the CIF.

Experimental details

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

Discussion

Alkyne units can function as rigid spacers between molecular fragments, whereas conjugation between the fragments is enabled by the two perpendicular π bonds. The π conjugation has attracted synthetic chemists for the construction of conjugated systems by coupling of α,ω-polyacetylenes to annulenes [2]. Due to their structural simplicity linear conjugated polyynes have been envisioned as molecular wires [3-6]. Meanwhile, diacetylene compounds are starting material for the synthesis of heterocyclic compounds. The molecular structure of 2-[6-(2-formylphenoxy)-2,4-hexadiynyloxy]benzaldehyde consists of a diacetylene moiety with two additional formyl groups and also two oxygens as hetero atoms. The condensation, namely the formation of the Schiff base, of salicylaldehyde derivatives with a diamine results in the well-known ligand salen. The coordination chemistry of this 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 [7,8]. Thus we envisioned to use 2-[6-(2-formylphenoxy)-2,4-hexadiynyloxy]benzaldehyde as starting material for the synthesis of some new Schiff bases. The analysis of the structure reveals that the distances in the aromatic rings are not completely uniform. The longest bond (140 pm) was found between the carbon atoms carrying the heterosubstituents. The shortest bonds are the next but one bonds on both sides. This pattern was found agreeing also in the structure of the corresponding monomeric alkyne 2-(2-propynyloxy)-benzaldehyde [1]. The molecules exhibit a crystallographically imposed inversion center. As expected the conjugated triple bond (120 pm) is found to be clearly longer than the isolated triple bond in the corresponding monomeric alkyne 2-(2-propynyloxy)benzaldehyde (117 pm, [1]). The bond length of the central *sp-sp* single bond amounts to 138 pm. The bond angles at these central *sp* centers exclusively bound to other sp centers are with 179° significantly closer to 180° than those additionally bound to a methylene group (175° resp. 177° in the corresponding monomeric alkyne [1]).

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* Correspondence author (e-mail: balalaie@kntu.ac.ir)

Table 1. Data collection and handling.

Crystal:	yellow polyhedron, size 0.05 × 0.21 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.93 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\max}$:	48.82°
$N(hkl)_{\mathrm{measured}}$, $N(hkl)_{\mathrm{unique}}$:	5840, 1273
Criterion for I_{obs}, $N(hkl)_{\mathrm{gt}}$:	$I_{\mathrm{obs}} > 2\ \sigma(I_{\mathrm{obs}})$, 835
$N(param)_{\mathrm{refined}}$:	109
Program:	SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.1635	0.3635	0.1267	0.069
H(3)	4*e*	0.4053	0.8076	0.2128	0.061
H(4)	4*e*	0.4957	0.8982	0.3672	0.069
H(5)	4*e*	0.4248	0.6960	0.4858	0.065
H(6)	4*e*	0.2681	0.3932	0.4524	0.055
H(9A)	4*e*	0.1720	–0.0189	0.3914	0.058
H(9B)	4*e*	0.0539	–0.0613	0.3213	0.058

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)	4*e*	0.2286(3)	0.4830(8)	0.1403(2)	0.064(2)	0.077(2)	0.035(2)	–0.007(2)	0.019(2)	–0.001(2)
O(1)	4*e*	0.2635(2)	0.5760(6)	0.0759(2)	0.097(2)	0.122(2)	0.037(1)	–0.028(2)	0.029(1)	0.005(1)
C(2)	4*e*	0.2825(2)	0.5471(7)	0.2388(2)	0.044(2)	0.048(2)	0.034(2)	0.004(1)	0.018(1)	–0.001(1)
C(3)	4*e*	0.3771(2)	0.7234(7)	0.2613(2)	0.056(2)	0.053(2)	0.050(2)	0.004(2)	0.025(2)	–0.001(2)
C(4)	4*e*	0.4307(3)	0.7784(8)	0.3525(2)	0.052(2)	0.062(2)	0.061(2)	–0.005(2)	0.019(2)	–0.020(2)
C(5)	4*e*	0.3884(3)	0.6563(8)	0.4226(2)	0.049(2)	0.070(2)	0.039(2)	0.014(2)	0.006(2)	–0.012(2)
C(6)	4*e*	0.2950(2)	0.4787(7)	0.4033(2)	0.050(2)	0.058(2)	0.031(2)	0.013(2)	0.014(1)	–0.001(2)
C(7)	4*e*	0.2405(2)	0.4264(6)	0.3107(2)	0.043(2)	0.040(2)	0.035(2)	0.009(1)	0.016(1)	–0.001(1)
O(8)	4*e*	0.1441(2)	0.2649(5)	0.2833(1)	0.049(1)	0.057(1)	0.034(1)	–0.003(1)	0.0178(9)	0.001(1)
C(9)	4*e*	0.1083(3)	0.0924(7)	0.3527(2)	0.060(2)	0.045(2)	0.049(2)	0.004(2)	0.029(2)	0.004(2)
C(10)	4*e*	0.0590(2)	0.2817(7)	0.4137(2)	0.052(2)	0.043(2)	0.040(2)	0.005(2)	0.021(1)	0.011(1)
C(11)	4*e*	0.0211(2)	0.4199(7)	0.4681(2)	0.050(2)	0.044(2)	0.042(2)	0.008(1)	0.023(1)	0.013(1)

Acknowledgments. S. B. is grateful to the Alexander von Humboldt foundation for a Research Fellowship and equipment donation. Partial support of this work by the K. N. Toosi University of Technology Research Council is gratefully acknowledged..

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