

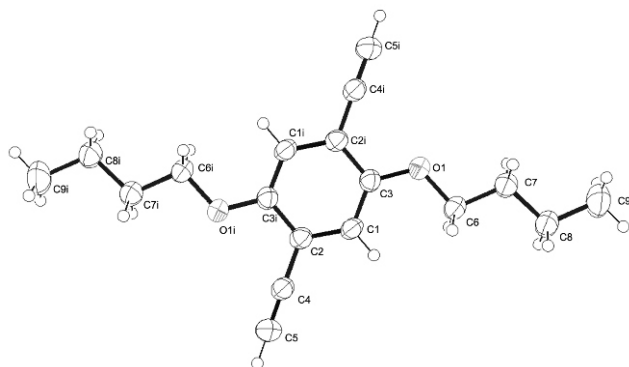
Crystal structure of 1,4-dibutoxy-2,5-diethynylbenzene, C₁₈H₂₂O₂

Shu-Hua He^I, Shi-Xu Yi^{II} and Jian Men^{*II}

^I School of Chemistry and Chemical Engineering, Yangtze Normal University, Fuling 408100, Chongqing, P. R. China

^{II} College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, P. R. China

Received February 28, 2011, accepted and available on-line June 24, 2011; CCDC no. 1267/3420



Abstract

C₁₈H₂₂O₂, monoclinic, *P*121/*c*1 (no. 14), *a* = 7.4576(5) Å, *b* = 17.5319(7) Å, *c* = 6.4822(4) Å, β = 109.011(6)°, *V* = 801.3 Å³, *Z* = 2, *R*_g(*F*) = 0.041, *wR*_{ref}(*F*²) = 0.115, *T* = 294 K.

Source of material

To the 1,4-dibromo-2,5-dibutoxybenzene (10.64 g, 28.01 mmol) in the presence of PdCl₂(PPh₃)₂ (0.02 g, 2.85·10^{−5} mmol), PPh₃ (0.04 g, 1.53·10^{−4} mmol) in a solution of Et₃N (140 ml) under an atmosphere of argon was added 3-methyl-1-butyn-3-ol (5.64 g, 67.19 mmol). After the mixture was heated to 333 K under an atmosphere of argon, CuI (0.04 g, 2.09·10^{−4} mmol) was added. Then, the mixture was refluxed for about 10 h (monitored by TLC) under an atmosphere of argon. The precipitate was filtered and washed with acetone (10 ml). After the solvent in the filtrate was removed, the residual solid was recrystallized from ethanol:water = 8:1 (V:V) to give colorless solid. To the solution of the obtained solid (2.71 g, 7.03 mmol) in toluene (42 ml) was added NaOH (1.40 g, 35.10 mmol) at 353 K and then the mixture was refluxed for 8 h (monitored by TLC), poured into 100 ml water and the organic layer was washed with dilute HCl (pH = 1–2), saturated NaCl solution and water to the pH = 7. After the solvent was removed, the residual solid was recrystallized from ethanol to give a yellow solid, m.p. 377–379 K (375–379 K [1]), yield 76 % based on the coupling product.

Discussion

The π -conjugated polymers have rapidly developed due to their potential applications in artificial photosynthesis [2], photocatalysis [3], molecular photovoltaic cells [4], molecular informatics [5], and optoelectronic devices [6]. Among them, linear poly(*p*-phenylenevinylene) (PPV) and polyphenyleneethynylene (PPE) are the outstanding representatives [7,8]. But

their applications are restricted by poor solubility. The commonly used strategy to enhance solubility is the introduction of lateral chains to the benzene ring [9]. So, the title compound is an important intermediate in synthesizing these polymers. Up to now, only the synthesis of the title compound has been reported [1]. But the crystal structure of it has not been reported in open literature.

The title compound has a symmetrical molecule. All of the carbon atoms and oxygen atoms are coplanar. The torsion angles C6–O1–C3–C2 and C6–O1–C3–C1 are 179.5(1)° and −0.15(8)°, respectively. The bond angles O1–C3–C2, O1–C6–C7 and C3–O1–C6 are 116.0(1)°, 108.2° and 118.2(9)°, respectively. *d*(O1–C3), *d*(O1–C6), *d*(C2–C4) and *d*(C4–C5) are 1.3637(1) Å, 1.4313(1) Å, 1.4375(2) Å and 1.1774(2) Å, respectively. So, the bond lengths and bond angles are well consistent with other related structures [9]. The unit cell packing is governed by van der Waals interaction, no other intermolecular interactions are observed.

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.36 × 0.40 × 0.42 mm
Wavelength:	Mo <i>K</i> _α radiation (0.7107 Å)
μ :	0.71 cm ^{−1}
Diffraction, scan mode:	Xcalibur, EOS, ω
$2\theta_{\max}$:	52.72°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	3542, 1639
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1155
<i>N</i> (<i>param</i>) _{refined} :	92
Programs:	SHELXS-97, SHELXL-97 [10], ORTEP-3 [11]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.6391	0.5433	0.2519	0.048
H(5)	4e	0.3373	0.7537	0.1594	0.061
H(6B)	4e	0.2377	0.5602	0.8874	0.052
H(6A)	4e	0.0797	0.5198	0.6961	0.052
H(7A)	4e	−0.0856	0.6355	0.6099	0.054
H(7B)	4e	0.0717	0.6758	0.8007	0.054
H(8B)	4e	−0.0096	0.5970	1.0529	0.062
H(8A)	4e	−0.1732	0.5612	0.8593	0.062
H(9A)	4e	−0.3175	0.6831	0.7874	0.125
H(9C)	4e	−0.1601	0.7143	0.9949	0.125
H(9B)	4e	−0.3050	0.6531	1.0195	0.125

* Correspondence author (e-mail: menjian@scu.edu.cn)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	4e	0.2366(1)	0.59242(5)	0.5933(2)	0.0597(6)	0.0438(5)	0.0600(6)	0.0090(5)	0.0381(5)	0.0087(4)
C(1)	4e	0.5834(2)	0.52572(7)	0.3522(2)	0.0468(8)	0.0388(7)	0.0403(7)	−0.0047(6)	0.0230(6)	0.0011(5)
C(2)	4e	0.4509(2)	0.57132(6)	0.4032(2)	0.0426(7)	0.0341(6)	0.0366(6)	−0.0048(5)	0.0152(5)	−0.0025(5)
C(3)	4e	0.3660(2)	0.54486(7)	0.5531(2)	0.0414(8)	0.0356(6)	0.0402(7)	−0.0012(6)	0.0182(6)	−0.0030(5)
C(4)	4e	0.4030(2)	0.64533(7)	0.3052(2)	0.0457(8)	0.0412(7)	0.0415(7)	−0.0040(6)	0.0206(6)	−0.0007(5)
C(5)	4e	0.3663(2)	0.70588(8)	0.2238(2)	0.062(1)	0.0406(7)	0.0561(8)	−0.0001(7)	0.0259(7)	0.0056(6)
C(6)	4e	0.1447(2)	0.56772(7)	0.7442(2)	0.0481(8)	0.0445(7)	0.0437(7)	−0.0002(6)	0.0242(6)	0.0012(5)
C(7)	4e	0.0050(2)	0.62800(7)	0.7546(2)	0.0450(8)	0.0442(7)	0.0495(8)	−0.0004(6)	0.0206(6)	−0.0005(6)
C(8)	4e	−0.1005(2)	0.60737(8)	0.9101(2)	0.0496(9)	0.0511(8)	0.0643(9)	−0.0008(7)	0.0306(7)	−0.0008(7)
C(9)	4e	−0.2329(3)	0.67022(9)	0.9298(4)	0.086(1)	0.070(1)	0.120(2)	0.011(1)	0.069(1)	−0.003(1)

Acknowledgments. This work was supported by FLKJ and the project number was 2010ABA1014. The authors thank Mr. Zhi-Hua Mao from Sichuan University for the X-Ray data collection.

References

- Chi, J. H.; Lee, C. L.; Kim, J. J.; Jung, J. C.: Synthesis and light-emitting properties of a novel π -conjugated poly[di(*p*-phenyleneethynylene)-alt-(*p*-phenyleneethynylene)] containing *n*-octyloxy side branches. *J. Appl. Poly. Sci.* **108** (2008) 9.
- Gust, D.; Moore, T. A.: Mimicking Photosynthesis. *Science* **244** (1989) 35-41.
- Ziessel, R. in: *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds* (Eds. K. Kalyanasundaram, M. Gratzel), p. 217. Kluwer Academic Publishers, Dordrecht, 1993.
- O'Regan, B.; Gratzel M.: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353** (1991) 737-740.
- Lin, H.; Huang, H.; He, Q.; Bai, F.: Photophysics and applications in plastic solar cells of conjugated polymer/fullerene composites. *Polym. Polym. Compos.* **11** (2003) 679-689.
- Barker, J. R. in: *Molecular Electronics* (Eds. M. C. Petty, M. R. Bryce, D. Bloor), p. 345. Edward Arnold, London 1995.
- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B.: Light-emitting diodes based on conjugated polymers. *Nature* **347** (1990) 539.
- Zhang, W.; Huang, P. C.: Synthesis and Optical Property Studies of Phenylacetylene meta-Connected Dendrimers. *Acta Chem. Sin.* **15** (2005) 1433.
- Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J.: Flexible light-emitting diodes made from soluble conducting polymers. *Nature* **357** (1992) 477.
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112-122.
- Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) *J. Appl. Crystallogr.* **30** (1997) 565.