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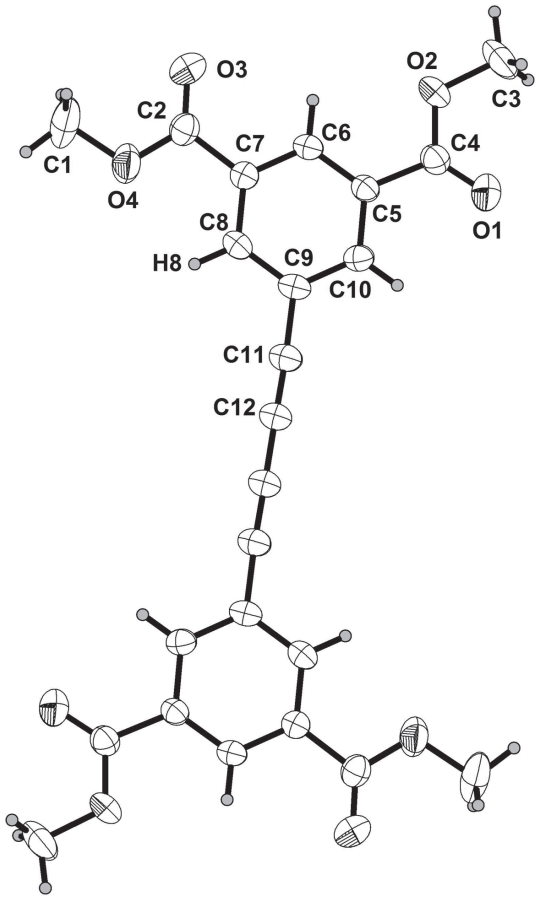
Crystal structure of tetramethyl 5,5′-(buta-1,3-diyne-1,4-diyl)diisophthalate, $C_{24}H_{18}O_8$



https://doi.org/10.1515/ncrs-2017-0228
Received August 24, 2017; accepted November 24, 2017; available online December 14, 2017

Abstract

$C_{24}H_{18}O_8$, monoclinic, $P2_1/n$ (no. 14), $a = 3.9930(7)$ Å, $b = 26.483(5)$ Å, $c = 10.3307(19)$ Å, $\beta = 98.136(4)°$, $V = 1081.5(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0606$, $wR_{ref}(F^2) = 0.1986$, $T = 293(2)$ K.

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CCDC no.: 1553277

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Needle, colourless
Size:	0.6 × 0.31 × 0.24 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	CCD Area Detector, ω-scans
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9034, 2681, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1989
$N(param)_{refined}$:	147
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.7794(5)	0.04450(7)	−0.14377(16)	0.0723(6)
O2	0.5086(5)	0.11679(6)	−0.19794(13)	0.0603(5)
O3	0.0968(5)	0.22627(7)	0.12699(19)	0.0717(5)
O4	0.1669(5)	0.20017(6)	0.33404(16)	0.0618(5)
C1	0.0156(8)	0.24672(11)	0.3716(3)	0.0817(9)
H1A	−0.2087	0.2499	0.3246	0.123*
H1B	0.1505	0.2749	0.3513	0.123*
H1C	0.0047	0.2462	0.4639	0.123*
C2	0.1960(5)	0.19550(7)	0.2078(2)	0.0434(4)
C3	0.5673(9)	0.10944(13)	−0.3316(2)	0.0819(9)
H3A	0.4425	0.1342	−0.3866	0.123*
H3B	0.4940	0.0762	−0.3601	0.123*
H3C	0.8043	0.1130	−0.3367	0.123*
C4	0.6322(5)	0.08110(7)	−0.11365(18)	0.0425(4)
C5	0.5708(4)	0.09276(6)	0.02249(15)	0.0346(4)
C6	0.4046(4)	0.13654(6)	0.05148(16)	0.0351(4)
H6	0.3186	0.1586	−0.0152	0.042*
C7	0.3674(4)	0.14736(6)	0.18014(16)	0.0350(4)
C8	0.4975(5)	0.11459(7)	0.27928(17)	0.0396(4)
H8	0.4735	0.1220	0.3655	0.048*
C9	0.6645(5)	0.07051(7)	0.25061(17)	0.0401(4)
C10	0.7004(5)	0.05963(7)	0.12121(17)	0.0379(4)
H10	0.8107	0.0303	0.1011	0.045*
C11	0.8065(5)	0.03868(8)	0.35587(18)	0.0471(5)
C12	0.9297(5)	0.01420(8)	0.44788(19)	0.0481(5)

Source of material

To remove oxygen, a 50 mL flask with a mixture of dry toluene (20 mL), copper(I) iodide (57.0 mg, 0.30 mmol), $Pd(PPh_3)_4$ (184 mg, 0.15 mmol), and triethylamine (5 mL) was deoxygened twice with N_2 and sealed. The mixture was stirred at 25 °C for 15 min, and then a solution of dimethyl 5-ethynylisophthalate (1.88 g, 4.31 mmol) dissolved in dry toluene (10 mL) was added dropwise. The mixture wasstirred for 4 h at 85 °C. The resulting solid was separated by filtration and dissolved in dichloromethane. The organic phase was washed with water and dried over anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane/ethyl acetate (5:1)) to provide a yellow solid (yield 65%) [4]. Colorless block crystals were obtained by slow evaporation at room temperature from dichloromethane and ethyl acetate in a 5:1 ratio.

Experimental details

All hydrogen atoms were placed in calculated positions and refined using a riding model. Methyl C—H bonds were fixed at 0.97 Å, with $U(H) = 1.5\,U_{eq}(C)$, and were allowed to spin about the C—C bond. Aromatic C—H distances were set to 0.95 Å and their U_{iso} set to 1.2 times the U_{eq} of the parent atom.

Discussion

In recent years, tetracarboxylate ligands, especially elongated tetracarboxylic acids, have been widely used in the construction of MOFs, including not only stable MOFs with large pores but also MOFs that are applicable in adsorption and storage of nitrogen, hydrogen, an methane [5–8]. In order to confirm the structure of the tetraacid, we obtained a single crystal structure of an important precursor.

The asymmetric unit of the title structure is one half of a molecule located around an inversion center (*cf*. the figure). Interestingly, the molecule is not completely planar molecule. The central two acetylene bonds are not in a straight line. Thus, the aryl moieties are twisted to each other. The title crystal structure has could contribute to the understanding of the true structure of graphite alkyne, which tends to belong to two-dimensional plane, or graphene has the quasi-two-dimensional structure with long-range fluctuation [9].

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