Xiang Huang and Da-Bin Shi*

Crystal structure of dimethyl 5-(10-(methoxycarbonyl)anthracen-9-yl) isophthalate, $C_{26}H_{20}O_6$

Table 1: Crystal collection and handling.

Crystal:	Block, yellow
Size:	$0.2 \times 0.2 \times 0.2$ mm
Wavelength:	Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å)
μ :	0.096 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon, ϕ and ω -scans
θ_{max} , completeness:	25.4° , 97%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13800, 3773, 0.0872
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1925
$N(\text{param})_{\text{refined}}$:	292
Programs:	Bruker programs [1], SHELX [2, 3]

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.

Source of material

Step 1:

Synthesis of 10-bromo-anthracene-9-carboxylic acid [4]. 9-anthracene carboxylic acid (4.0 g, 18 mmol) was dissolved in 300 mL of glacial acetic acid and cooled to 0°C prior to the dropwise addition of bromine (2 mL, 1.4 eq) over a period of 10 minutes. After complete addition of the bromine, the reaction mixture was allowed to warm to room temperature before stirring for 2 hours at 65°C and the crude product was precipitated *via* adding the acetic acid solution to 600 mL of ice/water slush, followed by suction filtration. The residue on the filter was dissolved in 500 mL 5% K_2CO_3 , followed by gravity filtration to remove undissolved side products. The filtrate was acidified with concentrated HCl to precipitate crude 10-bromo-anthracene-9-carboxylic acid, which was recrystallized from 100 mL ethanol to yield 5.76 g of yellow needles.

Step 2:

Synthesis of methyl 10-bromo-anthracene-9-carboxylate [5]. A 15 mL aliquot of SOCl_2 (0.21 mol) was placed in a N_2 -purged flask followed by the addition of 3.0 g (10 mmol) of 10-bromo-anthracene-9-carboxylic acid. One drop of anhydrous DMF

<https://doi.org/10.1515/ncrs-2018-0218>

Received June 26, 2018; accepted August 15, 2018; available online September 5, 2018

Abstract

$C_{26}H_{20}O_6$, monoclinic, $P2_1/n$ (no. 14), $a = 14.458(2)$ Å, $b = 9.4176(18)$ Å, $c = 16.914(3)$ Å, $\beta = 113.429(5)^\circ$, $V = 2113.1(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0676$, $wR_{\text{ref}}(F^2) = 0.1935$, $T = 173(2)$ K.

CCDC no.: 1843088

*Corresponding author: Da-Bin Shi, School of Pharmaceutical Sciences, Zunyi Medical University, Zunyi 563000, P.R. China, e-mail: sdb007.student@sina.com

Xiang Huang: School of Pharmaceutical Sciences, Zunyi Medical University, Zunyi 563000, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
O1	0.04448(19)	−0.1216(3)	0.06714(17)	0.0416(8)
O2	−0.06907(18)	−0.0372(3)	0.11518(16)	0.0418(8)
O3	0.1890(2)	0.3420(3)	0.43196(18)	0.0497(8)
O4	0.02858(19)	0.2756(3)	0.35943(17)	0.0436(8)
O5	0.7457(3)	0.2022(6)	0.3173(3)	0.131(2)
O6	0.6861(2)	0.1026(4)	0.1928(3)	0.0794(12)
C1	0.0235(3)	−0.0466(4)	0.1158(2)	0.0292(9)
C2	−0.1462(3)	−0.1216(5)	0.0498(3)	0.0490(12)
H2A	−0.1575	−0.0846	−0.0074	0.073
H2B	−0.2091	−0.1164	0.0587	0.073
H2C	−0.1239	−0.2206	0.0542	0.073
C3	0.0982(3)	0.0430(4)	0.1838(2)	0.0272(9)
C4	0.1961(3)	0.0482(4)	0.1876(2)	0.0261(9)
H4	0.2121	−0.0022	0.1460	0.031
C5	0.2706(2)	0.1253(4)	0.2508(2)	0.0241(8)
C6	0.2468(2)	0.1970(4)	0.3120(2)	0.0263(9)
H6	0.2979	0.2473	0.3571	0.032
C7	0.1483(3)	0.1956(4)	0.3078(2)	0.0274(9)
C8	0.0739(3)	0.1182(4)	0.2436(2)	0.0290(9)
H8	0.0069	0.1168	0.2408	0.035
C9	0.1262(3)	0.2777(4)	0.3733(2)	0.0315(9)
C10	−0.0001(3)	0.3555(5)	0.4193(3)	0.0563(13)
H10A	0.0381	0.3210	0.4780	0.084
H10B	−0.0724	0.3432	0.4046	0.084
H10C	0.0145	0.4564	0.4159	0.084
C11	0.3756(2)	0.1316(4)	0.2526(2)	0.0254(9)
C12	0.3942(2)	0.2193(4)	0.1933(2)	0.0254(8)
C13	0.3169(3)	0.3027(4)	0.1307(2)	0.0332(9)
H13	0.2502	0.2977	0.1284	0.040
C14	0.3358(3)	0.3884(5)	0.0748(3)	0.0417(11)
H14	0.2825	0.4403	0.0328	0.050
C15	0.4348(3)	0.4002(5)	0.0793(3)	0.0487(12)
H15	0.4480	0.4626	0.0408	0.058
C16	0.5112(3)	0.3250(5)	0.1368(3)	0.0452(11)
H16	0.5772	0.3359	0.1385	0.054
C17	0.4945(3)	0.2287(4)	0.1958(2)	0.0331(10)
C18	0.5714(3)	0.1449(4)	0.2554(2)	0.0342(10)
C19	0.5521(3)	0.0534(4)	0.3121(2)	0.0312(9)
C20	0.4523(3)	0.0480(4)	0.3116(2)	0.0259(8)
C21	0.4354(3)	−0.0433(4)	0.3714(2)	0.0336(9)
H21	0.3707	−0.0448	0.3736	0.040
C22	0.5091(3)	−0.1285(5)	0.4257(3)	0.0422(11)
H22	0.4954	−0.1891	0.4646	0.051
C23	0.6057(3)	−0.1271(5)	0.4242(3)	0.0474(12)
H23	0.6566	−0.1884	0.4615	0.057
C24	0.6268(3)	−0.0391(5)	0.3700(3)	0.0426(11)
H24	0.6928	−0.0390	0.3706	0.051
C25	0.6768(3)	0.1550(5)	0.2599(3)	0.0480(12)
C26	0.7869(4)	0.1088(7)	0.1915(4)	0.097(2)
H26A	0.8215	0.1950	0.2211	0.146
H26B	0.7808	0.1103	0.1317	0.146
H26C	0.8258	0.0252	0.2209	0.146

was added to start the reaction. After 5 min, the solid dissolved completely. The temperature was increased to 60 °C, and the reaction mixture was kept overnight under stirring.

Upon reaction completion, unreacted SOCl₂ was evaporated under reduced pressure. The acyl chloride was used without further characterization. Subsequently, a methanol (30 mL) solution of acyl chloride was stirred under an atmosphere of nitrogen at 80 °C for 6 h. After the reaction was complete, the solvent was rotary-evaporated, and CH₂Cl₂ (60 mL) and H₂O (60 mL) were added. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (40 mL). The organic phase was combined, washed with saturated NaHCO₃ aqueous solution and brine subsequently, dried over anhydrous MgSO₄, and filtered. Removal of the volatile solvent gave the target compound (3.0 g, 95%).

Step 3:

Synthesis of dimethyl 5-bromo-benzene-1,3-dicarboxylate [6]. 5-amino-isophthalic acid dimethyl ester (5 g) was dissolved in 120 mL of 15% hydrobromic acid and cooled to 5 °C. NaNO₂ (12 mL, 2.5 M) was introduced slowly by rapid stirring, giving a solution of diazonium bromide. The solution of diazonium bromide was added to a solution containing 5 g of CuBr and 45 mL of 15% of hydrobromic acid under stirring, and the temperature was kept under 5 °C. After the addition was completed, it was kept stirring under room temperature for 2 h. The organic layer was separated and washed three times with water, dried with MgSO₄, filtered, and concentrated in a vacuum. The crude product was purified by column chromatography to obtain the target compound as a brown powder (5.7 g, 88%).

Synthesis of dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate [6]. The mixture of dimethyl 5-bromo-benzene-1,3-dicarboxylate (2 g, 7.3 mmol), bis(pinacolato)diborane (2.2 g, 8.7 mmol), potassium acetate (2.4 g, 24.5 mmol), Pd(dppf)₂Cl₂ (0.1 g, 0.14 mmol) and dried 1,4-dioxane (20 mL) was stirred at 100 °C overnight and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with Na₂SO₃ and the solvent was removed in a vacuum. The crude product was purified by column chromatography to obtain the target compound as a colorless powder (1.7 g, 75%).

Step 4:

Synthesis of the title compound [7]. A mixture of methyl 10-bromo-anthracene-9-carboxylate (1.0 g, 3.2 mmol), dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (1.6 g, 5 mmol), K₂CO₃ (3.0 g, 22 mmol) and Pd(PPh₃)₄ (0.08 g, 0.05 mmol, 2 mol%), in 100 mL of dioxane/H₂O (5/1) was stirred under nitrogen for 12 h at 90 °C. After the mixture was cooled to room temperature, it was extracted with CH₂Cl₂ and washed with H₂O three times. The organic layer was then dried with MgSO₄, and the solvent was removed. The resulting crude product was purified by column chromatography using silica gel and methylene chloride as

the eluent. Dimethyl 5-(10-(methoxycarbonyl)anthracen-9-yl) isophthalate was obtained after removal of the solvents (1.2 g, 88% yield). The crystal suitable for X-ray analysis was obtained by slow evaporation of ethanol and dioxane at room temperature over a period of 7 days.

Experimental details

The structure was solved by Direct Methods [2] using the SHELX-2014 program package [3]. Hydrogen atoms were placed in geometrically idealized positions and refined using a riding model.

Discussion

Design and synthesis of intriguing metal-organic frameworks (MOFs) have become a hot spot in inorganic chemistry. There are significant application materials in the field of gas adsorption, molecular sieves, fluorescence, magnetism, and catalysis [8–12]. The design process is influenced extremely by ligands [13]. During the self-assembly process, the addition of mixed ligands has become an impactful method. Furthermore, the lengths of organic ligands play a crucial role in determining the effective porosity. Multi-carboxylic ligands are spiffy in this aspect due to their multiple coordination modes [14]. To the best of our knowledge this molecule has not been used to construct MOFs so far.

The title compound consists of one substituted phenyl moiety and one substituted anthracenyl moiety. The dihedral angle between the planes of the two aromatic ring systems is 68.7° . Bond lengths and bond angles within the molecule are in agreement with the values reported for related compounds. The bond lengths of C1–O1 and C1–O2 are 1.210(4) Å and 1.338(4) Å, respectively. And the bond lengths of C9–O3 and C9–O4 are 1.208(4) Å and 1.336(4) Å, respectively. Furthermore, the bond lengths of C25–O5 and C25–O6 are 1.167(5) Å and 1.291(5) Å, respectively. The bond length of C5–C3 is 1.506(5) Å, which is slightly shorter than that of typical C–C bond length (1.53 Å). The bond length of C1–C3 and C7–C9 are 1.488(5) Å and 1.486(5) Å. The bond angle (C1–O2–C2) and (O1–C1–O2) are $115.6(3)^\circ$ and $123.6(3)^\circ$, respectively. And the bond angle (C9–O4–C10) and (O3–C9–O4) are $116.5(3)^\circ$ and $123.2(3)^\circ$, respectively. Moreover, the bond angle (C25–O6–C26) and (O5–C25–O6) are $116.7(4)^\circ$ and $121.6(4)^\circ$, respectively. In the crystal van der Waals interactions are effective in the molecular packing.

Acknowledgements: We are grateful for financial support from National Natural Science Foundation of China (grant no. 21362047) and Science and Technology Foundation of

Guizhou Province (grant no. QKHSYZ-2013-3061 and QKHJZ-2014-2175).

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2004).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: SHELXT-integrated space-group and crystal structure determination. *Acta Crystallogr. A* **71** (2015) 3–8.
4. Zhu, L.; Al-Kaysi, R. O.; Dillon, R. J.; Tham, F. S.; Bardeen C. J.: Crystal structures and photophysical properties of 9-anthracene carboxylic acid derivatives for photomechanical applications. *Cryst. Growth Des.* **11** (2011) 4975–4983.
5. Umeda, R.; Nishimura, T.; Kaiba, K.; Tanaka, T.; Takahashi, Y.; Nishiyama Y.: Rhenium complex-catalyzed acylative cleavage of ethers with acyl chlorides. *Tetrahedron* **67** (2011) 7217–7221.
6. Chen, Z.; Xiang, S.; Liao, T.; Yang, Y.; Chen, Y.-S.; Zhou, Y.; Zhao, D.; Chen, B.: A new multidentate hexacarboxylic acid for the construction of porous metal-organic frameworks of diverse structures and porosities. *Cryst. Growth Des.* **10** (2010) 2775–2779.
7. Shi, D.; Ren, Y.; Jiang, H.; Cai, B.; Lu, J.: Synthesis, structures, and properties of two three-dimensional metal-organic frameworks, based on concurrent ligand extension. *Inorg. Chem.* **51** (2012) 6498–6506.
8. Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M.: Multiple functional groups of varying ratios in metal-organic frameworks. *Science* **327** (2010) 846–850.
9. Yoon, M.; Srirambalaji, R.; Kim, K.: Homochiral metal-organic frameworks for asymmetric heterogeneous catalysis. *Chem. Rev.* **112** (2012) 1196–1231.
10. Yang, Y. S.; Wang, K. Z.; Yan, D. P.: Lanthanide doped coordination polymers with tunable afterglow based on phosphorescence energy transfer. *Chem. Commun.* **53** (2017) 7752–7755.
11. Yang, Y. S.; Wan, K. Z.; Yan, D. P.: Smart luminescent coordination polymers toward multimode logic gates: time-resolved, tribochromic and excitation-dependent fluorescence/phosphorescence emission. *ACS Appl. Mater. Inter.* **9** (2017) 17399–17407.
12. Yang, X. G.; Yan, D. P.: Long-afterglow metal-organic frameworks: reversible guest induced phosphorescence tenability. *Chem. Sci.* **7** (2016) 4519–4526.
13. Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M.; Rizzato, S.: Complex interwoven polymeric frames from the self-assembly of silver cations and sebaconitrile. *Chem. Eur. J.* **5** (1999) 5237–5243.
14. Xue, M.; Zhu, G. S.; Li, Y. X.: Structure, hydrogen storage, and luminescence properties of three 3D metal-organic frameworks with NbO and PtS topologies. *Cryst. Growth Des.* **8** (2008) 2478–2483.