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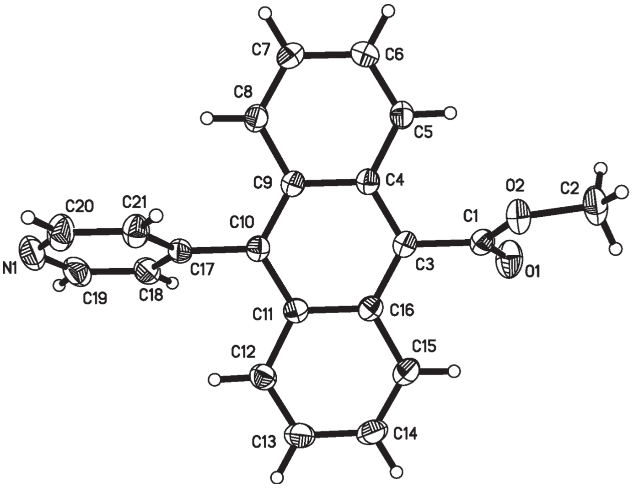
Crystal structure of methyl 10-(pyridin-4-yl)-anthracene-9-carboxylate, $C_{21}H_{15}NO_2$



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Abstract

$C_{21}H_{15}NO_2$, orthorhombic, *Aba*2 (no. 41), $a = 22.149(2)$ Å, $b = 13.2899(12)$ Å, $c = 10.6679(10)$ Å, $V = 3140.2(5)$ Å^3, $Z = 8$, $R_{\mathrm{gt}}(F) = 0.0418$, $wR_{\mathrm{ref}}(F^2) = 0.0953$, $T = 296(2)$ K.

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The asymmetric unit of the title 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:	Block, colorless
Size:	$0.30 \times 0.20 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$\theta_{\max}$, completeness:	27.6°, >99%
$N(hkl)_{\mathrm{measured}}$, $N(hkl)_{\mathrm{unique}}$, R_{int}:	9199, 3516, 0.027
Criterion for I_{obs}, $N(hkl)_{\mathrm{gt}}$:	$I_{\mathrm{obs}} > 2\ \sigma(I_{\mathrm{obs}})$, 2700
$N(param)_{\mathrm{refined}}$:	218
Programs:	Bruker programs [1], SHELX [2, 3]

Source of material

The title compound 10-bromo-anthracene-9-carboxylic acid was prepared following a modified literature procedure [4]. A solution of 9-anthracene carboxylic acid (5.0 g, 22.5 mmol) in 300 mL glacial acetic acid was cooled to 0 °C before slowly adding a solution of bromine in acetic acid (2 mL Br_2 in 20 mL acetic acid, 1.7 eq) over a period of 10 min. The reaction mixture was allowed to warm to room temperature before stirring for 2 h at 65 °C. Crude 10-bromo-anthracene-9-carboxylic acid was precipitated by adding the acetic acid solution to 800 mL of ice/water slush, followed by suction filtration. The residue on the filter was dissolved in 500 mL of a 5% aquaeus solution of K_2CO_3 followed by gravity filtration to remove undissolved side products such as 9,10-dibromoanthracene. 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.

Methyl 10-bromo-anthracene-9-carboxylate was prepared following a modified literature procedure [5]. To 10-bromo-anthracene-9-carboxylic acid (5.2 g, 17.3 mmol) in methanol (150 mL), was added concentrated H_2SO_4 (5 mL). The solution was refluxed for 24 h under a nitrogen atmosphere. After the solution was cooled to room temperature, the solvent was evaporated, and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The organic phase was combined, washed with saturated $NaHCO_3$ aqueous solution and brine subsequently, dried over anhydrous $MgSO_4$, and filtered. Removal of the volatile solvent gave the target compound (4.89 g, 97%).

Synthesis of the title compound [6]. A mixture of methy-10-bromo-anthracene-9-carboxylate (4.0 g, 12.7 mmol), 4-pyridineboronic acid (2.5 g, 20 mmol), K_2CO_3 (6.0 g, 44 mmol) and palladium tetrakis(triphenylphosphine) (0.3 g, 0.2 mmol, 2 mol%) as catalyst, in 120 mL of dioxane/H_2O (5/1) was stirred under nitrogen for 12 h at 90 °C. After the mixture was cooled to room temperature, it was extracted with CH_2Cl_2 and washed with H_2O three times. The organic layer was then dried with $MgSO_4$, and the

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.24325(7)	0.78833(11)	0.19861(18)	0.0673(5)
O2	0.31337(6)	0.73032(10)	0.06820(15)	0.0515(4)
N1	0.51268(10)	1.32958(16)	0.2050(2)	0.0721(6)
C1	0.29025(8)	0.79925(15)	0.14515(19)	0.0405(4)
C2	0.27588(11)	0.64369(15)	0.0421(3)	0.0668(7)
H2A	0.2414	0.6642	−0.0060	0.100*
H2B	0.2627	0.6143	0.1196	0.100*
H2C	0.2987	0.5951	−0.0046	0.100*
C3	0.33011(8)	0.89035(14)	0.15521(17)	0.0367(4)
C4	0.34093(8)	0.94926(13)	0.04840(18)	0.0363(4)
C5	0.31460(9)	0.92650(14)	−0.07049(19)	0.0436(5)
H5	0.2898	0.8704	−0.0783	0.052*
C6	0.32510(10)	0.98493(17)	−0.1718(2)	0.0506(5)
H6	0.3075	0.9687	−0.2484	0.061*
C7	0.36263(10)	1.07055(16)	−0.1623(2)	0.0497(5)
H7	0.3699	1.1099	−0.2328	0.060*
C8	0.38794(9)	1.09561(14)	−0.0516(2)	0.0430(5)
H8	0.4123	1.1525	−0.0471	0.052*
C9	0.37836(8)	1.03699(14)	0.05870(18)	0.0359(4)
C10	0.40366(8)	1.06310(13)	0.17571(18)	0.0361(4)
C11	0.39301(9)	1.00331(14)	0.28179(17)	0.0372(4)
C12	0.42026(9)	1.02408(15)	0.40032(19)	0.0457(5)
H12	0.4457	1.0794	0.4079	0.055*
C13	0.41011(11)	0.96570(17)	0.5018(2)	0.0545(6)
H13	0.4283	0.9811	0.5780	0.065*
C14	0.37185(11)	0.88130(17)	0.4920(2)	0.0562(6)
H14	0.3646	0.8420	0.5625	0.067*
C15	0.34558(9)	0.85645(16)	0.3819(2)	0.0483(5)
H15	0.3210	0.7998	0.3776	0.058*
C16	0.35497(9)	0.91576(14)	0.27209(18)	0.0378(4)
C17	0.44183(8)	1.15498(14)	0.18710(19)	0.0395(4)
C18	0.42376(10)	1.23683(15)	0.2585(2)	0.0501(5)
H18	0.3872	1.2353	0.3015	0.060*
C19	0.46039(13)	1.32060(18)	0.2653(2)	0.0631(7)
H19	0.4478	1.3741	0.3150	0.076*
C20	0.52981(10)	1.2511(2)	0.1371(3)	0.0661(7)
H20	0.5663	1.2553	0.0943	0.079*
C21	0.49683(10)	1.16340(16)	0.1258(2)	0.0515(5)
H21	0.5114	1.1104	0.0776	0.062*

solvent was removed with a rotary evaporator. The resulting crude product was purified by column chromatography using silica gel and methylene chloride as the eluent. Methyl 10-(pyridin-4-yl)-anthracene-9-carboxylate was obtained after removal of the solvents (3.4 g, 85% yield). Melting point: 114–115 °C. The crystal suitable for X-ray analysis was obtained by slow evaporation of an anhydrous ethanol and dioxane at room temperature over a period of seven days, yield: 0.68 g (90.5%).

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. The structure was solved by direct methods [2] and refined on F^2 by full-matrix least-squares technique using the SHELX program package [3].

Discussion

Nowadays, there has been increasing research on the crystal engineering of metal-organic frameworks (MOFs), also known as coordination polymer (CPs), for their unusual topology frameworks as well as their potential applications in gas storage and separation [7, 8], catalysis [9, 10], sensing [11] and magnetic applications [12]. Many different rigid ligands with multicoordination sites have been used to build these stable frameworks. At present, pyridine carboxylic acid (Hpydc) seems to be a potential rigid ligand in some complexes reported. *O*- and *N*-donors of Hpydc allow the construction of many different kinds of interesting three-dimensional structures of transition metal and lanthanide complexes [13, 14]. Herein, we reported a new compound, namely 10-(pyridin-4-yl)anthracene-9-carboxylate, which may be hydrolyzed and deprotonized to produce 10-(pyridin-4-yl)-9-anthroate, which has not been used to construct MOFs so far.

The title compound consists of one pyridyl moiety and one substituted anthracenyl moiety. The dihedral angle between the planes of two aromatic rings is 65.7°. Bond lengths and bond angles within the molecular system are in agreement with the values reported. The bond lengths of C1—O1 and C1—O2 are 1.198(2) Å and 1.332(3) Å, respectively. The bond length of C1—C3 and C10—C17 are 1.503(3) Å and 1.489(3) Å, which are insignificantly shorter than that of typical C—C bond length. The bond angle (C1—O2—C2) and (O1—C1—O2) are 116.42(17)° and 123.10(19)°, respectively. In the crystal packing, dipole-dipole and van der Waals interactions are effective in the molecular packing.

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