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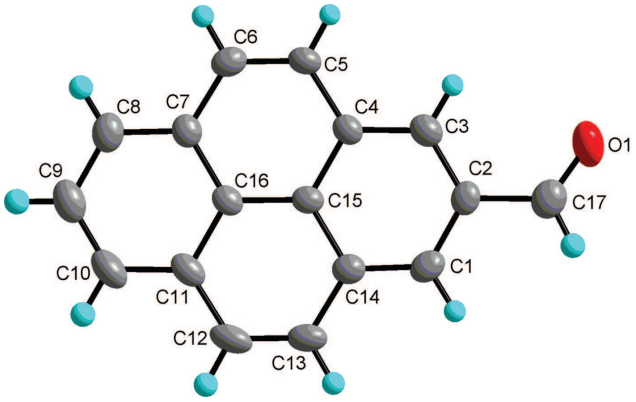
Crystal structure of pyrene-2-carbaldehyde, $C_{17}H_{10}O$



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Abstract

$C_{17}H_{10}O$, monoclinic, $P2_1/c$ (no. 14), $a = 8.1312(16)$ Å, $b = 7.8252(16)$ Å, $c = 17.231(3)$ Å, $\beta = 92.47(3)°$, $V = 1095.3(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0517$, $wR_{ref}(F^2) = 0.1281$, $T = 293(2)$ K.

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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

All chemicals were purchased from commercial sources and used as received without further purification. The title complex was prepared by two steps. The intermediate 2-formyl-4,5,9,10-tetrahydropyrene was prepared by the following procedure: To a stirred solution of 4,5,9,10-tetrahydropyrene (2.060 g, 10 mmol) and dichloromethyl methyl ether (1.495 g, 13 mmol) in CH_2Cl_2 (80 mL) was added at 0 °C a solution of titanium tetrachloride (10.95 mL, 100 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 3 h at room temperature. The mixture was poured into ice-water and extracted with CH_2Cl_2 two times. The organic layer was washed with

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.15 × 0.14 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, ω-scans
θ_{max}, completeness:	26°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7793, 2121, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma\,(I_{obs})$, 1133
$N(param)_{refined}$:	162
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.9439(2)	0.2050(2)	−0.10678(9)	0.0507(5)
C1	0.5362(3)	0.2907(2)	−0.04617(12)	0.0326(6)
H1	0.5026	0.3529	−0.0900	0.039*
C2	0.6942(3)	0.2235(2)	−0.04090(12)	0.0292(5)
C3	0.7474(3)	0.1309(2)	0.02406(12)	0.0315(6)
H3	0.8537	0.0869	0.0269	0.038*
C4	0.6443(3)	0.1027(2)	0.08490(11)	0.0268(5)
C5	0.6931(3)	0.0038(2)	0.15243(12)	0.0288(5)
H5	0.7988	−0.0418	0.1566	0.035*
C6	0.5892(3)	−0.0239(3)	0.20932(12)	0.0326(6)
H6	0.6252	−0.0880	0.2522	0.039*
C7	0.4241(3)	0.0420(2)	0.20639(11)	0.0300(5)
C8	0.3144(3)	0.0129(3)	0.26496(13)	0.0384(6)
H8	0.3470	−0.0537	0.3076	0.046*
C9	0.1562(3)	0.0824(3)	0.26035(14)	0.0438(6)
H9	0.0848	0.0638	0.3002	0.053*
C10	0.1054(3)	0.1797(3)	0.19605(13)	0.0406(6)
H10	−0.0002	0.2257	0.1936	0.049*
C11	0.2095(3)	0.2094(2)	0.13542(13)	0.0325(6)
C12	0.1593(3)	0.3056(3)	0.06735(14)	0.0388(6)
H12	0.0533	0.3503	0.0631	0.047*
C13	0.2631(3)	0.3320(3)	0.00954(13)	0.0345(6)
H13	0.2268	0.3947	−0.0338	0.041*
C14	0.4269(3)	0.2667(2)	0.01291(12)	0.0286(5)
C15	0.4810(3)	0.1715(2)	0.07997(12)	0.0257(5)
C16	0.3715(3)	0.1419(2)	0.14055(11)	0.0263(5)
C17	0.8042(3)	0.2533(3)	−0.10544(14)	0.0403(6)
H17	0.7620	0.3140	−0.1482	0.048*

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water, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography using hexane/ CH_2Cl_2 as an eluent to afford 2.0358 g 2-formyl-4,5,9,10-tetrahydropyrene in 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.62 (s, 2H), 7.23 (d, $J = 6.8$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 2H), 2.97 (dd, $J = 9.4$, 3.6 Hz, 8H). **GC/MS MS**: ($C_{17}H_{14}O$) m/z 234(M^+, 78), 216(18), 205(100), 189(38), 101(20).

The title compound was synthesized by dehydrogenation of the intermediate 2-formyl-4,5,9,10-tetrahydropyrene a solution of 2-formyl-4,5,9,10-tetrahydropyrene (1.170 g, 5 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.951 g, 13 mmol) in 100 mL of freshly-dried benzene was refluxed for two days. After removing the solvent by rotary evaporation, the residue was purified by silica gel chromatography using hexane/CH_2Cl_2 as an eluent to afford 1.081 g 2-pyrenyl aldehyde in 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.68 (s, 2H), 8.27 (d, $J = 7.6$ Hz, 2H), 8.23–8.16 (m, 4H), 8.15–8.11 (m, 1H). **GC—MS MS**: ($C_{17}H_{10}O$) m/z 230(M^+, 100), 201(95), 100(35). The yellow block crystals of the title compound were obtained by slow evaporation of hexane/CH_2Cl_2 solution (v:v = 1/1) and the selected crystal was structurally characterized by X-ray diffraction analysis.

Experimental details

All H atoms bond to C atoms were introduced using the HFIX commond in the SHELXL program [2], with the value of 0.93 Å or 0.96 Å for C—H bonds distances. All H atoms were allowed for as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ for hydrogen atoms. The structure was checked using PLATON [3].

Discussion

In the last several decades, the research on organic fluorescent materials has gained important momentum due to their wide range of applications in organic light-emitting diodes (OLED), organic field effect transistor (OFET), organic lasers, fluorescent sensors and solar cells, etc. [4–8]. As a well known fluorophore, pyrene and its derivatives have been paid much attentions due to their pure blue fluorescence with high quantum yield, exceptionally long fluorescence lifetime, excellent thermal stability, and high charge carrier mobility [9–11]. Generally, the derivatization of pyrene is the key step for interesting pyrene-based functional materials. However, the active position of direct electrophilic mono substitution reaction on pyrene is almost exclusively at the electron-rich 1-position of pyrene [12–15]. Compared to the derivatives with the substitutents at the 1-position of pyrene, the compounds with the substituents at 2-position are relatively limited, and only a few 2-substituted pyrenes (2-bromopyrene, 2-amionpyrrene, 2-acetylpyrene, and so on) have been obtained up to date [16–19]. Recently, we synthesized one important pyrene-based derivative 2-pyrenyl aldehyde through the formylation and aromatization using 4,5,9,10-tetrahydropyrene as the starting material.

The single X-ray diffraction analysis agrees well with expected structure of the title compound. The functional group of aldehyde locates at the 2-position of pyrene. The C–O bond length is 1.198(3) Å, which is the typical double bond distance of aldehyde group. The C2–C17 bond length is 1.476(3) Å, indicating the π–π conjugation effect between the pyrene π-ring system and the aldehyde functional group. All carbon and oxygen atoms are nearly in a strict plane with the largest deviation to be 0.031(3) Å from the mean plane based on all the atoms. There is relatively strong intermolecular π–π interaction between adjacent molecules with the shortest interatomic distance is 3.366(3) Å, forming dimeric supramolecular structures. In addition, there exist weak intermolecular C–H$\cdots\pi$ and C–H$\cdots$O interactions, which link the units of the title compounds into three-dimensional structure.

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