Miao Bao-Xi, Zhang Li-Fang and Zhao Yun*

Crystal structure of pyrene-4-aldehyde, C₁₇H₁₀O

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.18 × 0.16 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX II, φ and ω
$\theta_{\max}$, completeness:	27.5°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8542, 2430, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1957
$N(\text{param})_{\text{refined}}$:	163
Programs:	SHELX [1], PLATON [2]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.08571(11)	0.73278(15)	−0.11159(8)	0.0413(3)
C1	0.21356(16)	0.70645(18)	−0.10688(11)	0.0312(3)
H1	0.2292	0.6473	−0.1567	0.037*
C2	0.35103(15)	0.75278(16)	−0.03459(9)	0.0225(3)
C3	0.35280(14)	0.85347(15)	0.04612(9)	0.0207(3)
C4	0.22445(15)	0.92042(17)	0.06338(10)	0.0257(3)
H4	0.1313	0.8990	0.0223	0.031*
C5	0.23448(16)	1.01847(17)	0.14111(10)	0.0287(3)
H5	0.1479	1.0619	0.1513	0.034*
C6	0.37110(16)	1.05240(17)	0.20352(10)	0.0267(3)
H6	0.3753	1.1184	0.2551	0.032*
C7	0.50348(15)	0.98879(16)	0.19010(9)	0.0222(3)
C8	0.64717(16)	1.02360(17)	0.25327(9)	0.0265(3)
H8	0.6531	1.0916	0.3043	0.032*
C9	0.77384(16)	0.95971(18)	0.24020(9)	0.0268(3)
H9	0.8651	0.9828	0.2829	0.032*
C10	0.76971(14)	0.85646(16)	0.16119(9)	0.0227(3)
C11	0.89839(15)	0.78834(18)	0.14545(10)	0.0274(3)
H11	0.9906	0.8074	0.1882	0.033*
C12	0.89127(15)	0.69253(18)	0.06709(10)	0.0289(3)
H12	0.9784	0.6488	0.0579	0.035*
C13	0.75612(15)	0.66206(17)	0.00307(10)	0.0262(3)
H13	0.7529	0.5989	−0.0494	0.031*
C14	0.62341(15)	0.72504(16)	0.01608(9)	0.0209(3)
C15	0.48051(15)	0.69448(16)	−0.04799(9)	0.0232(3)
H15	0.4759	0.6322	−0.1010	0.028*
C16	0.62911(14)	0.82350(15)	0.09584(9)	0.0191(3)
C17	0.49502(14)	0.88801(15)	0.11076(8)	0.0194(3)

<https://doi.org/10.1515/ncrs-2018-0254>

Received July 20, 2018; accepted September 8, 2018; available online September 27, 2018

Abstract

C₁₇H₁₀O, monoclinic, *P*2₁/*c* (no. 14), *a* = 9.3121(19) Å, *b* = 8.0958(16) Å, *c* = 14.944(3) Å, β = 106.06(3)°, *V* = 1082.7(4) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0488, *wR*_{ref}(*F*²) = 0.1418, *T* = 293(2) K.

CCDC no.: 1866559

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.

*Corresponding author: Zhao Yun, School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, P.R. China, e-mail: zhanglifang@cumt.edu.cn

Miao Bao-Xi and Zhang Li-Fang: School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, P.R. China

Source of material

All chemicals were purchased from commercial sources and used as received. The title compound was prepared

by two steps. The intermediate 4-cyanopyrene was prepared by the following procedures. To a 100 mL two-necked flask, 4-bromopyrene (0.327 g, 1.164 mmol), CuCN (0.215 g, 2.4 mmol), and anhydrous DMF (30 mL) were added. The mixture was heated at 160 °C for 3 days, and then cooled down to 90 °C. Subsequently, a mixture of ethylenediamine (10 mL) and water (15 mL) was added. The resulting mixture was stirred at 90 °C for 3 h and then cooled to room temperature. The product was extracted with dichloromethane three times and the organic layer was dried over magnesium sulfate, filtered, and evaporated. A quantity of 0.2 g (76% yield) of C₁₇H₉N was isolated as pale green crystals. IR (KBr): 3043 cm⁻¹, 2220 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.66–8.55 (m, 2H), 8.41–8.25 (m, 3H), 8.22–8.06 (m, 4H). GC/MS MS: (C₁₇H₉N) m/z 227(M⁺, 100), 200(16), 100(20).

The title compound was synthesized by dehydrogenation of the above intermediate 4-cyanopyrene: an oven-dried 50 mL flask which was equipped with a side arm, a condenser, and adapter was flushed with nitrogen and charged with 0.150 g (0.66 mmol) of 4-cyanopyrene and 30 mL of CH₂Cl₂. The solution was cooled to 0 °C in an ice-water bath and 0.8 mL of 1 M solution of DIBAL-H in n-hexane was added slowly with stirring. After 15 min, additional 0.8 mL of 1 M solution of DIBAL-H in n-hexane was added slowly. The mixture was stirred for 3 h at room temperature. The mixture was poured into 50% sulfuric acid water solution and extracted with CH₂Cl₂ two times. The organic layer was washed with water, dried over MgSO₄ and concentrated in vacuo. The residue was purified by silica gel chromatography using hexane/CH₂Cl₂ as an eluent to afford 0.1 g pyrene-4-aldehyde in 66% yield. IR (KBr): 2724 cm⁻¹, 1686 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.55 (d, J = 0.9 Hz, 1H), 9.64 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 1.2 Hz, 1H), 8.35 (d, J = 7.7 Hz, 2H), 8.29 (d, J = 7.6 Hz, 1H), 8.22–8.02 (m, 4H). GC/MS MS: (C₁₇H₁₀O) m/z 230(M⁺, 60), 202(100), 100(25). The yellow block crystals of the title compound were obtained by slow evaporation of hexane/CH₂Cl₂ solution (v:v = 1/1).

Experimental details

All H atoms bond were introduced using the HFIX command in the SHELXL program [1]. All H atoms were allowed for as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The structure was checked using PLATON [2].

Comment

Since its discovery in 1837 [3], pyrene as one of the most known polyaromatic hydrocarbons (PAHs) has been paid much attention in the development of organic fluorescent materials [4–6]. In the last decades, numerous investigations have been carried out on the design and synthesis of

pyrene-based materials with a broad range of potential applications such as organic light-emitting diodes (OLED), organic field effect transistor (OFET), organic lasers, chemosensors and solar cells, etc. [7–11], due to their pure blue fluorescence with high quantum yield, exceptionally long fluorescence lifetime, excellent thermal stability, and high charge carrier mobility. In order to obtain excellent pyrene-based functional materials, much efforts have been made to modify its molecular structure by introducing suitable electron-donating or -accepting groups at different positions of the pyrene. The formyl group is a useful substituent group for interesting pyrene-based functional materials [12]. Generally, a direct formylation on the pyrene ring occurs almost exclusively at the electron rich 1-position of pyrene [13]. Nevertheless, pyrene-2-aldehyde have been successfully designed and synthesized through the formylation and aromatization using 4,5,9,10-tetrahydropyrene as the starting material and its crystal structure has been reported by our group recently [14]. As part of our work on pyrene-based derivatives, we synthesized pyrene-4-aldehyde using a new effective strategy through reduction of 4-cyanopyrene from 4-bromopyrene.

The single X-ray diffraction analysis shows the expected structure of the title compound pyrene-4-aldehyde. The aldehyde group locates at the 4-position of the pyrene. The C–O bond length is 1.1923(18) Å, similar to that of our previously reported pyrene-2-aldehyde [14]. The C1–C2 bond length is 1.4770(19) Å, indicating the π – π conjugation effect between the pyrene and the aldehyde group. All the carbon and oxygen atoms are nearly in a strict plane with the largest deviation 0.062(2) Å. The supramolecular structure is also comparable with that of its isomer pyrene-2-aldehyde [14]. Firstly, two molecules of the title compound form a dimeric unit by relatively strong π – π interactions with the shortest interatomic distance of 3.359(2) Å. These dimeric structures are linked into a three-dimensional structure by weak C–H··· π and C–H···O interactions.

Acknowledgements: This work was supported by the Fundamental Research Funds for the Central Universities (2017BSCXA05).

References

- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7–13.
- Laurent, A.: Pyrene from coal tar. *Ann. Chim. Phys.* **66** (1837) 136–137.
- Zhang, R.; Sun, H.; Zhao, Y.; Tang, X. X.; Ni, Z. H.: Dipolar 1,3,6,8-tetrasubstituted pyrene-based blue emitters containing electro-transporting benzimidazole moieties:

- syntheses, structures, optical properties, electrochemistry and electroluminescence. *Dyes Pigments* **152** (2018) 1–13.
5. Figueira-Duarte, T. M.; Mullen, K.: Pyrene-based materials for organic electronics. *Chem. Rev.* **111** (2011) 7260–7314.
 6. Zhang, R.; Zhao, Y.; Zhang, L. F.; Xu, L.; Ni, Z. H.: A series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrene-based green and blue emitters with 4-*tert*-butylphenyl and aramine attachments. *Dyes Pigments* **130** (2016) 106–115.
 7. Zhang, R.; Zhao, Y.; Zhang, L. F.; Xu, L.; Ni, Z. H.: A series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrene-based green and blue emitters with 4-*tert*-butylphenyl and aramine attachments. *Dyes Pigments* **130** (2016) 106–115.
 8. Oniwa, K.; Kikuchi, H.; Shimotani, H.; Ikeda, S.; Asao, N.; Yamamoto, Y.; Tanigaki, K.; Jin, T. N.: 2-Positional pyrene end-capped oligothiophenes for high performance organic field effect transistors. *Chem. Commun.* **52** (2016) 4800–4803.
 9. Yi, J. P.; Zhao, L.; Xu, W. D.; Liu, C. F.; Lai, W. Y.; Huang, W.: Pyrene-capped starburst emitters as gain media for organic lasers: design, synthesis, and stabilized lasing properties. *J. Mater. Chem. C* **4** (2016) 7546–7553.
 10. Chu, K. H.; Zhou, Y.; Fang, Y.; Wang, L. H.; Li, J. Y.; Yao, C.: Rhodamine-pyrene conjugated chemosensors for ratiometric detection of Hg^{2+} ions: different sensing behavior between a spirolactone and a spirothiolactone. *Dyes Pigments* **98** (2013) 339–346.
 11. Liu, X.; Luo, G. P.; Cai, X. Y.; Wu, H. B.; Su, S. J.; Cao, Y.: Pyrene terminal functionalized perylene diimide as non-fullerene acceptors for bulk heterojunction solar cells. *RSC Adv.* **5** (2015) 83155–83163.
 12. Liu, Y. F.; Jun, E. J.; Kim, G.; Lee, A. R.; Lee, J. H.; Yoon, J.: A bispyrene derivative as a selective fluorescent probe for RNA. *Chem. Commun.* **50** (2014) 2505–2507.
 13. Yamato, T.; Fujimoto, M.; Nagano, Y.: Electrophilic substitution of 7-*tert*-butyl-1-substituted pyrenes. A new route for the preparation of 1,3-disubstituted pyrenes. *Org. Prep. Proceed. Int.* **29** (1997) 320–330.
 14. Miao, B. X.; Tang, X. X.; Zhang, L. F.: Crystal structure of pyrene-2-carbaldehyde, $C_{17}H_{10}O$. *Z. Kristallogr. NCS* **233** (2018) 655–657.