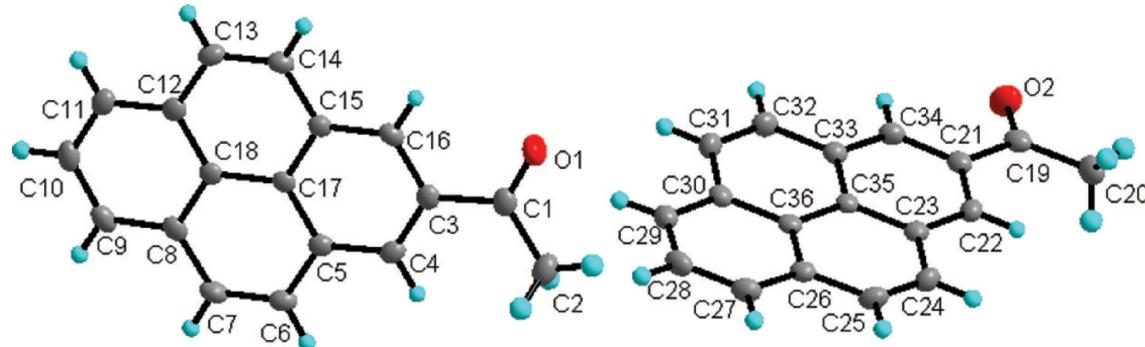


Yun-Hui Xu*, Bao-Xi Miao and Ran Zhang

Crystal structure of 2-acetyl pyrene, $C_{18}H_{12}O$



<https://doi.org/10.1515/ncks-2018-0432>

Received October 15, 2018; accepted November 6, 2018; available online December 5, 2018

Abstract

$C_{18}H_{12}O$, triclinic, $P\bar{1}$ (no. 2), $a = 8.0788(16)$ Å, $b = 8.1221(16)$ Å, $c = 18.162(4)$ Å, $\alpha = 91.01(3)$ °, $\beta = 94.62(3)$ °, $\gamma = 92.80(3)$ °, $V = 1186.2(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0415$, $wR_{ref}(F^2) = 0.1044$, $T = 293(2)$ K.

CCDC no.: 1877283

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.

Source of material

The title complex was prepared by two steps. The intermediate 2-acetyl-4,5,9,10-tetrahydronaphthalene was prepared by the following procedures using 4,5,9,10-tetrahydronaphthalene as the starting materials. To a solution of 4,5,9,10-tetrahydronaphthalene (2.065 g, 10 mmol) in CS₂ (50 mL) was added anhydrous AlCl₃ (3.000 g, 22.6 mmol) at 0 °C under nitrogen atmosphere. Then, acetyl chloride (0.942 g, 12 mmol) in CS₂ (20 mL) was added into the mixture. The resulting solution was allowed to warm to room temperature with stir-

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.12 × 0.10 × 0.09 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{\max} , completeness:	27.5°, >96%
$N(hkl)$ _{measured} , $N(hkl)$ _{unique} , R_{int} :	9811, 5236, 0.030
Criterion for I_{obs} , $N(hkl)$ _{gt} :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3554
$N(\text{param})$ _{refined} :	345
Programs:	Bruker programs [1], SHELX [2], PLATON [3]

ring for 2 h. The reaction mixture was poured into a large amount of ice-water 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 2.0358 g 2-acetyl-4,5,9,10-tetrahydronaphthalene in 87% yield. **1H NMR** (400 MHz, CDCl₃) δ 7.71 (s, 2H), 7.25–7.18 (m, 1H), 7.14 (d, $J = 7.4$ Hz, 2H), 3.03–2.89 (m, 8H), 2.64 (m, 3H). **GC/MS MS:** (C₁₇H₁₄O) *m/z* 248(M^+ , 78), 233(100), 202(40), 189(38), 101(20).

The title compound was synthesized by dehydrogenation of the above intermediate 2-acetyl-4,5,9,10-tetrahydronaphthalene as following: a solution of 2-acetyl-4,5,9,10-tetrahydronaphthalene (1.220 g, 5 mmol) and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone; 2.456 g, 10.8 mmol) in 30 mL of freshly-dried benzene was refluxed for 24 h. After removing the solvent by rotary evaporation, the residue was purified by silica gel chromatography using hexane/CH₂Cl₂ as an eluent to afford 0.8295 g 2-acetyl pyrene in 70% yield. **1H NMR** (400 MHz, CDCl₃) δ 8.75 (s, 2H), 8.23 (d, $J = 7.6$ Hz, 2H), 8.18–8.11 (m, 4H), 8.09 (t, $J = 7.6$ Hz, 1H), 2.93 (s, 3H). **GC–MS MS:** (C₁₈H₁₂O) *m/z*

*Corresponding author: Yun-Hui Xu, School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, P.R. China; and School of Materials Engineering, Xuzhou College of Industrial Technology, Xuzhou 221140, P.R. China, e-mail: 165666296@qq.com

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

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O	0.42960(11)	0.38553(12)	0.30956(5)	0.0376(3)
C1	0.28051(16)	0.40460(14)	0.29848(7)	0.0242(3)
C2	0.18566(17)	0.33315(16)	0.23005(7)	0.0320(3)
H2A	0.1467	0.4208	0.1995	0.048*
H2B	0.0925	0.2656	0.2435	0.048*
H2C	0.2571	0.2673	0.2033	0.048*
C3	0.19304(14)	0.50183(14)	0.35263(6)	0.0204(3)
C4	0.02616(15)	0.53773(14)	0.34070(6)	0.0213(3)
H4	-0.0345	0.5001	0.2975	0.026*
C5	-0.05170(14)	0.62978(13)	0.39294(6)	0.0193(3)
C6	-0.22224(14)	0.67189(14)	0.38139(7)	0.0232(3)
H6	-0.2848	0.6361	0.3383	0.028*
C7	-0.29334(14)	0.76301(14)	0.43230(7)	0.0237(3)
H7	-0.4036	0.7897	0.4231	0.028*
C8	-0.20320(14)	0.81921(13)	0.49988(7)	0.0207(3)
C9	-0.27348(15)	0.91417(14)	0.55333(7)	0.0244(3)
H9	-0.3841	0.9410	0.5458	0.029*
C10	-0.18043(16)	0.96841(14)	0.61703(7)	0.0261(3)
H10	-0.2290	1.0320	0.6517	0.031*
C11	-0.01602(15)	0.92960(14)	0.63003(7)	0.0240(3)
H11	0.0446	0.9676	0.6732	0.029*
C12	0.05997(15)	0.83398(13)	0.57906(6)	0.0200(3)
C13	0.22973(15)	0.79079(14)	0.59050(7)	0.0222(3)
H13	0.2916	0.8248	0.6340	0.027*
C14	0.30195(14)	0.70170(14)	0.53955(7)	0.0213(3)
H14	0.4125	0.6759	0.5486	0.026*
C15	0.21154(14)	0.64613(13)	0.47181(6)	0.0184(3)
C16	0.28345(14)	0.55645(13)	0.41794(6)	0.0203(3)
H16	0.3948	0.5322	0.4256	0.024*
C17	0.04138(14)	0.68408(13)	0.45911(6)	0.0174(3)
C18	-0.03427(14)	0.77894(13)	0.51280(6)	0.0178(3)
O2	0.98724(12)	0.39056(11)	-0.11701(5)	0.0375(3)
C19	0.94771(15)	0.24356(16)	-0.12047(7)	0.0253(3)
C20	0.97948(16)	0.14184(16)	-0.18766(7)	0.0306(3)
H20A	1.0405	0.2084	-0.2204	0.046*
H20B	0.8753	0.1029	-0.2126	0.046*
H20C	1.0429	0.0495	-0.1727	0.046*
C21	0.86550(14)	0.16276(14)	-0.05876(6)	0.0215(3)
C22	0.81227(14)	-0.00294(14)	-0.06272(6)	0.0217(3)
H22	0.8299	-0.0656	-0.1045	0.026*
C23	0.73298(14)	-0.07711(14)	-0.00534(6)	0.0204(3)
C24	0.68088(15)	-0.24882(15)	-0.00707(7)	0.0249(3)
H24	0.6988	-0.3138	-0.0481	0.030*
C25	0.60640(15)	-0.31797(15)	0.04964(7)	0.0256(3)
H25	0.5755	-0.4299	0.0471	0.031*
C26	0.57390(14)	-0.22296(14)	0.11365(6)	0.0215(3)
C27	0.49717(15)	-0.29220(15)	0.17318(7)	0.0264(3)
H27	0.4658	-0.4040	0.1719	0.032*
C28	0.46770(15)	-0.19600(16)	0.23379(7)	0.0271(3)
H28	0.4160	-0.2437	0.2727	0.033*
C29	0.51423(14)	-0.02933(16)	0.23735(7)	0.0253(3)
H29	0.4919	0.0338	0.2783	0.030*
C30	0.59444(14)	0.04514(14)	0.18010(6)	0.0214(3)
C31	0.65270(15)	0.21562(15)	0.18326(7)	0.0253(3)
H31	0.6340	0.2808	0.2241	0.030*

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C32	0.73406(15)	0.28286(14)	0.12800(7)	0.0245(3)
H32	0.7730	0.3925	0.1323	0.029*
C33	0.76171(14)	0.18907(14)	0.06277(6)	0.0207(3)
C34	0.84056(14)	0.25702(14)	0.00396(7)	0.0224(3)
H34	0.8772	0.3675	0.0066	0.027*
C35	0.70488(13)	0.01993(14)	0.05784(6)	0.0185(3)
C36	0.62354(13)	-0.05232(14)	0.11713(6)	0.0194(3)

230(M^+ , 100), 201(95), 100(35). The yellow block crystals of the title compound were obtained by slow evaporation of methanol/CH₂Cl₂ solution (v:v = 1/10).

Experimental details

All H atoms bond to C atoms were introduced using the HFIX command in the SHELXL program [2], with the values of 0.93 Å or 0.96 Å for C—H bonds distances, respectively. All H atoms were allowed for as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for hydrogen atoms, respectively. The structure was checked using PLATON [3].

Discussion

Pyrene derivatives have attracted significant attention due to their excellent fluorescence properties, such as high fluorescence quantum yield, outstanding thermal stability, long fluorescence lifetime [4–7]. Many interesting pyrene-based functional materials have been reported to be used as important organic semiconductors for the applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic devices (OPVs) [8–11]. However, the derivatization of pyrene almost focus on 1-position, or 1-, 3-, 6-, and 8-positions [12–15]. There are few reports concerning 2-substituted pyrene derivatives due to its hard synthesis [16–18]. That is because the presence of the nodal plane in the HOMO and LUMO locates perpendicular to the molecule and passes through the 2-position. Herein, we report the synthesis and crystal structure of a compound which involves substitution at the 2-position of the pyrene core.

The single X-ray diffraction analysis agrees well with expected structure of the title compound 2-acetyl pyrene C₁₈H₁₂O. There are two independent 2-acetyl pyrene molecules in the asymmetric unit of the title crystal structure. The acetyl functional group is located at the 2-position of pyrene. The C—O bond lengths are 1.2229(15) Å and 1.2200(14) Å, respectively in the two independent 2-acetyl pyrene molecules, which is the typical double bond distance of an acetyl group. The C1—C3 and C19—C21 bond lengths are

1.4931(17) Å and 1.4937(17) Å, respectively, which are slightly smaller than those C1—C2 and C19—C20 bond lengths, indicating the π — π conjugation effect between pyrenyl moiety and the carbonyl group. All the carbon and oxygen atoms are nearly in a strict plane with the largest deviation 0.116(2) Å and 0.048(2) Å from the mean plane based on all the atoms for the two independent 2-acetyl pyrene molecules, respectively. The dihedral angle of the mean planes based on two 2-acetyl pyrene molecules is 80.65(12)°. Bond lengths and angles are all in the expected ranges and similar to those in the parent structure [19]. There are relatively strong intermolecular π — π interactions between adjacent molecules with the shortest interatomic distance is 3.349(2) Å for two 2-acetyl pyrene molecules in which C1—O1 bond is located, and 3.349(2) Å for another two 2-acetyl pyrene molecules in which C19—O2 bond is located, forming two different dimeric structures [20]. In addition, there exist weak intermolecular C—H··· π and C—H···O interactions, which link the units of the title compounds into three-dimensional structure.

Acknowledgements: This work was supported by the funding research projects of Jiangsu Province 333 high-level talents (BRA2016459).

References

1. Bruker. APEX3, SAINT-Plus, XPREP. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
3. Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7–13.
4. Stylianou, K. C.; Heck, R.; Chong, S. Y.; Bacsa, J.; Jones, J. T. A.; Wong, K. S.; Khimyak, Y. Z.; Bradshaw, D.; Rosseinsky, M. J.: A guest-responsive fluorescent 3D microporous metal-organic framework derived from a long-lifetime pyrene core. *J. Am. Chem. Soc.* **132** (2010) 4419–4130.
5. Figueira-Duarte, T. M.; Müllen, K.: Pyrene-based materials for organic electronics. *Chem. Rev.* **111** (2011) 7260–7314.
6. Sasabe, H.; Kido, J.: Multifunctional materials in high-performance OLEDs: challenges for solid-state lighting. *Chem. Mater.* **23** (2010) 621–630.
7. Gingras, M.; Placide, V.; Raimundo, J. M.; Bergamini, G.; Ceroni, P.; Balzani, V.: Polysulfurated pyrene-cored dendrimers: luminescent and electrochromic properties. *Chem. Eur. J.* **14** (2008) 10357–10363.
8. Huang, J.; Tang, R.; Zhang, T.; Li, Q.; Yu, G.; Xie, S.; Liu, Y.; Ye, S.; Qin, J.; Li, Z.: A new approach to prepare efficient blue AIE emitters for undoped OLEDs. *Chemistry* **20** (2014) 5317–5326.
9. Chercka, D.; Yoo, S. J.; Baumgarten, M.; Kim, J. J.; Müllen, K.: Pyrene based materials for exceptionally deep blue OLEDs. *J. Mater. Chem. C.* **2** (2014) 9083–9086.
10. Liu, Y.; Shan, T.; Yao, L.; Bai, Q.; Guo, Y.; Li, J.; Han, X.; Li, W.; Wang, Z.; Yang, B.; Lu, P.; Ma, Y.: Isomers of pyrene-imidazole compounds: synthesis and configuration effect on optical properties. *Org. Lett.* **17** (2015) 6138–6141.
11. Niko, Y.; Sasaki, S.; Narushima, K.; Sharma, D. K.; Vacha, M.; Konishi, G.: 1-, 3-, 6-, and 8-Tetrasubstituted asymmetric pyrene derivatives with electron donors and acceptors: high photostability and regioisomer-specific photophysical properties. *J. Org. Chem.* **80** (2015) 10794–10805.
12. 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 arylamine attachments. *Dyes Pigm.* **130** (2016) 106–115.
13. Zhang, R.; Zhang, T. F.; Xu, L.; Han, F. F.; Zhao, Y.; Ni, Z. H.: A new series of short axially symmetrically and asymmetrically 1,3,6,8-tetrasubstituted pyrenes with two types of substituents: syntheses, structures, photophysical properties and electroluminescence. *J. Mol. Struct.* **1127** (2017) 237–246.
14. Hu, J. Y.; Feng, X.; Tomiyasu, H.; Seto, N.; Rayhan, U.; Elsegood, M. R. J.; Redshaw, C.; Yamato, T.: Synthesis and fluorescence emission properties of 1,3,6,8-tetraarylpyrenes. *J. Mol. Struct.* **1047** (2013) 194–203.
15. Zhang, R.; Han, F. F.; Zhang, L. F.: Crystal structure of 2-(4-methylbenzoyl)pyrene, C₂₄H₁₆O. Z. *Kristallogr. NCS* **231** (2016) 855–857.
16. Laali, K. K.; Arrica, M. A.; Okazaki, T.; Bunge, S. D.: Synthesis and stable-ion studies of regioisomeric acetyl nitropyrenes and nitropyrenyl carbinols and giao-dft study of nitro substituent effects on α -pyrenyl carbocations. *Eur. J. Org. Chem.* **36** (2008) 6093–6105.
17. Cabral, L. I. L.; Henriques, M. S. C.; Paixão, J. A.; Cristiano, M. L. S.: Synthesis and structure of 2-substituted pyrene-derived scaffolds. *Tetra. Lett.* **58** (2017) 4547–4550.
18. Suzuki, S.; Takeda, T.; Kuratsu, M.; Kozaki, M.; Sato, K.; Shiomi, D.; Takui, T.; Okada, K.: Pyrene-dihydrophenazine bis(radical cation) in a singlet ground state. *Org. Lett.* **11** (2009) 2816–2818.
19. Bao-Xi, M.; Xin-Xue, T.; Li-Fang, Z.: Crystal structure of pyrene-2-carbaldehyde, C₁₇H₁₀O. Z. *Kristallogr. NCS* **233** (2018) 655–657.
20. Martinez, C. R.; Iverson, B. L.: Rethinking the term “p-stacking”. *Chem. Sci.* **3** (2012) 2191–2201.