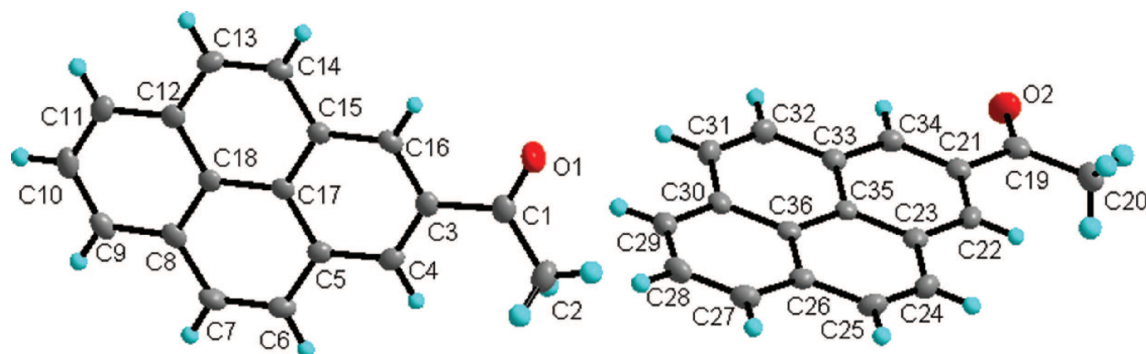


Yun-Hui Xu\*, Bao-Xi Miao and Ran Zhang

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

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## 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,  $\alpha = 91.01(3)^\circ$ ,  $\beta = 94.62(3)^\circ$ ,  $\gamma = 92.80(3)^\circ$ ,  $V = 1186.2(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.0415$ ,  $wR_{ref}(F^2) = 0.1044$ ,  $T = 293(2)$  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.

## Source of material

The title complex was prepared by two steps. The intermediate 2-acetyl-4,5,9,10-tetrahydropyrene was prepared by the following procedures using 4,5,9,10-tetrahydropyrene as the starting materials. To a solution of 4,5,9,10-tetrahydropyrene (2.065 g, 10 mmol) in  $CS_2$  (50 mL) was added anhydrous  $AlCl_3$  (3.000 g, 22.6 mmol) at 0 °C under nitrogen atmosphere. Then, acetyl chloride (0.942 g, 12 mmol) in  $CS_2$  (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:	$0.12 \times 0.10 \times 0.09$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
$\mu$ :	$0.08\text{ mm}^{-1}$
Diffractometer, scan mode:	Bruker APEX-II, $\varphi$ and $\omega$ -scans
$\theta_{max}$ , completeness:	$27.5^\circ$ , >96%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	9811, 5236, 0.030
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2\sigma(I_{obs})$ , 3554
$N(param)_{refined}$ :	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  $CH_2Cl_2$  two times. The organic layer was washed with 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-acetyl-4,5,9,10-tetrahydropyrene in 87% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  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: ( $C_{17}H_{14}O$ )  $m/z$  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-tetrahydropyrene as following: a solution of 2-acetyl-4,5,9,10-tetrahydropyrene (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/ $CH_2Cl_2$  as an eluent to afford 0.8295 g 2-acetyl pyrene in 70% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  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: ( $C_{18}H_{12}O$ )  $m/z$

\*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 (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
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	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
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*<sup>+</sup>, 100), 201(95), 100(35). The yellow block crystals of the title compound were obtained by slow evaporation of methanol/CH<sub>2</sub>Cl<sub>2</sub> 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*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(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 C<sub>18</sub>H<sub>12</sub>O. 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  $\pi$ – $\pi$  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  $\pi$ – $\pi$  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 $\cdots$  $\pi$  and C–H $\cdots$ O interactions, which link the units of the title compounds into three-dimensional structure.

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