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Synthesis and crystal structure of 4-acetylpirene, $C_{18}H_{12}O$

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Abstract

$C_{18}H_{12}O$, triclinic, $P\bar{1}$ (no. 2), $a = 10.132(2)$ Å, $b = 10.654(2)$ Å, $c = 11.730(2)$ Å, $\alpha = 90.31(3)^\circ$, $\beta = 102.38(3)^\circ$, $\gamma = 104.81(3)^\circ$, $V = 1193.2(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0403$, $wR_{\text{ref}}(F^2) = 0.1037$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure is shown in Figure. Table 1 contains crystallographic data and Table 2 contains the 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.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.10 × 0.08 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffraction, scan mode:	BRUKER APEX II, φ and ω
θ_{max} , completeness:	27.5°, 97%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9761, 5251, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3742
$N(\text{param})_{\text{refined}}$:	345
Programs:	BRUKER [1], SHELX [2], PLATON [3]

The title compound was prepared by two steps using 1,2,3,6,7,8-hexahydrypyrene as the starting material. 0.427 g (3.2 mmol) of anhydrous $AlCl_3$ and 30 mL of dichloromethane were added into a 100 mL three port flask at 0 °C. An amount of 0.251 g (3.2 mmol) acetyl chloride was dissolved in 10 mL dichloromethane, and the solution was added drop by drop into the flask under the protection of nitrogen and magnetic stirring. After the addition, the mixed solution was cooled to room temperature until it became clear, and then transferred to the low temperature bath. An amount of 0.56 g (2.7 mmol) of 1,2,3,6,7,8-hexahydrypyrene dissolved in 20 mL dichloromethane was added drop by drop into the reaction solution. After the addition, it was moved to room temperature for 2 h. Then, the reaction

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	0.59444 (9)	0.16236 (9)	0.05203 (8)	0.0343 (2)
C1	0.66692 (12)	0.19276 (11)	−0.01931 (10)	0.0234 (3)
C2	0.60684 (13)	0.23671 (14)	−0.13607 (11)	0.0337 (3)
H2A	0.5078	0.2239	−0.1451	0.051*
H2B	0.6239	0.1870	−0.1972	0.051*
H2C	0.6504	0.3273	−0.1405	0.051*
C3	0.81763 (11)	0.19112 (11)	0.00927 (9)	0.0193 (3)
C4	0.91177 (11)	0.28638 (11)	−0.03050 (9)	0.0200 (3)
H4	0.8785	0.3441	−0.0808	0.024*
C5	1.05921 (11)	0.30121 (11)	0.00188 (9)	0.0185 (2)
C6	1.15481 (12)	0.40113 (11)	−0.03725 (10)	0.0233 (3)
H6	1.1225	0.4617	−0.0845	0.028*
C7	1.29674 (12)	0.41111 (12)	−0.00663 (11)	0.0267 (3)
H7	1.3591	0.4781	−0.0335	0.032*
C8	1.34681 (12)	0.32185 (12)	0.06384 (10)	0.0246 (3)
H8	1.4426	0.3294	0.0833	0.029*
C9	1.25569 (11)	0.22064 (11)	0.10624 (9)	0.0197 (3)
C10	1.30359 (12)	0.12492 (12)	0.17701 (10)	0.0228 (3)
H10	1.3990	0.1309	0.1979	0.027*
C11	1.21295 (12)	0.02645 (12)	0.21375 (10)	0.0226 (3)
H11	1.2473	−0.0344	0.2592	0.027*
C12	1.06446 (12)	0.01286 (11)	0.18461 (9)	0.0193 (3)
C13	0.96960 (12)	−0.08923 (11)	0.22113 (10)	0.0231 (3)
H13	1.0024	−0.1508	0.2667	0.028*
C14	0.82800 (12)	−0.10031 (11)	0.19074 (10)	0.0247 (3)
H14	0.7664	−0.1692	0.2162	0.030*
C15	0.77563 (12)	−0.01004 (11)	0.12252 (10)	0.0222 (3)
H15	0.6795	−0.0198	0.1023	0.027*
C16	0.86579 (11)	0.09525 (10)	0.08394 (9)	0.0178 (2)
C17	1.01284 (11)	0.10661 (10)	0.11494 (9)	0.0162 (2)
C18	1.10954 (11)	0.21003 (10)	0.07529 (9)	0.0171 (2)
O2	−0.37033 (9)	0.14448 (9)	0.55836 (8)	0.0350 (2)
C19	−0.29545 (12)	0.14518 (11)	0.48936 (10)	0.0226 (3)
C20	−0.35154 (12)	0.06341 (12)	0.37635 (10)	0.0285 (3)
H20A	−0.3068	−0.0061	0.3781	0.043*
H20B	−0.3329	0.1162	0.3126	0.043*
H20C	−0.4508	0.0278	0.3660	0.043*
C21	−0.14643 (11)	0.22500 (11)	0.51765 (9)	0.0187 (2)
C22	−0.04921 (12)	0.17927 (11)	0.47795 (9)	0.0201 (3)
H22	−0.0796	0.1039	0.4287	0.024*
C23	0.09716 (12)	0.24236 (11)	0.50888 (10)	0.0200 (3)
C24	0.19561 (12)	0.19259 (12)	0.47034 (10)	0.0266 (3)
H24	0.1662	0.1157	0.4233	0.032*
C25	0.33696 (13)	0.25644 (14)	0.50134 (12)	0.0334 (3)
H25	0.4017	0.2222	0.4752	0.040*
C26	0.38188 (13)	0.37103 (14)	0.57113 (11)	0.0326 (3)
H26	0.4770	0.4126	0.5917	0.039*
C27	0.28734 (12)	0.42572 (12)	0.61139 (10)	0.0254 (3)
C28	0.32979 (14)	0.54629 (13)	0.68121 (11)	0.0314 (3)
H28	0.4243	0.5901	0.7022	0.038*
C29	0.23609 (13)	0.59723 (12)	0.71692 (10)	0.0292 (3)
H29	0.2672	0.6758	0.7616	0.035*
C30	0.08917 (13)	0.53329 (11)	0.68770 (9)	0.0236 (3)
C31	−0.00893 (14)	0.58545 (12)	0.72430 (10)	0.0286 (3)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H31	0.0205	0.6649	0.7676	0.034*
C32	−0.14908 (14)	0.52042 (12)	0.69705 (10)	0.0292 (3)
H32	−0.2130	0.5561	0.7230	0.035*
C33	−0.19622 (13)	0.40255 (12)	0.63146 (10)	0.0244 (3)
H33	−0.2913	0.3606	0.6139	0.029*
C34	−0.10292 (12)	0.34554 (11)	0.59116 (9)	0.0193 (3)
C35	0.04227 (12)	0.41232 (11)	0.61981 (9)	0.0188 (3)
C36	0.14259 (11)	0.35991 (11)	0.58090 (9)	0.0195 (3)

solution was poured into 50 mL 10% hydrochloric acid solution for hydrolysis. After 2 h, the solution was separated. The aqueous layer was extracted three times with 20 mL dichloromethane and the organic phase was combined. The organic phase was washed with saturated NaCl solution and deionized water for three times, dried with anhydrous MgSO₄, and dried to obtain light yellow solid. Using petroleum ether and dichloromethane as eluent, 0.5535 g of white solid was obtained through silica gel column. Yield: 81%, melting point: 71–73 °C. **FTIR** (KBr): 3045, 1675, 1597, 1558, 1419, and 1351 cm^{−1}. **¹H NMR** (400 MHz, CDCl₃): 7.40 (s, 1H), 7.22 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 6.1 Hz, 2H), 3.10 (dt, *J* = 9.2, 6.1 Hz, 6H), 2.67 (s, 3H), 2.17–1.95 (m, 4H). **GC-MS**: (C₁₈H₁₈O) *m/z* 250(M⁺, 100), 235(85), 207(70), 191(40), 179(42), 101(18).

The title compound was synthesized by dehydrogenation of the above intermediate 4-acetyl-1,2,3,6,7,8-hexahydropyrene as following: 0.29 g (1.16 mmol) of 4-acetyl-1,2,3,6,7,8-hexahydropyrene, 0.9216 g (4.06 mmol) of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) and 30 mL of toluene were added into a 50 mL double flask with reflux device, the reaction mixture was heated and refluxed for 6 h under the protection of nitrogen. After the reaction, the filtrate was filtered, collected and dried. The solid was dissolved in 50 mL dichloromethane, washed with 5% NaOH solution and deionized water for three times, respectively, dried with anhydrous MgSO₄, and rotary evaporated to obtain brown solid. Using dichloromethane and petroleum ether as eluent, 0.2182 g yellow plate crystals were obtained by silica gel column separation and purification. Yield: 77%, melting point: 135–138 °C. Structural analysis: **FTIR** 3045, 1675, 1597, 1558, 1419, and 1351 cm^{−1}. **¹H NMR** (400 MHz, CDCl₃): 7.40(s, 1H), 7.22 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 6.1 Hz, 2H), 3.10 (dt, *J* = 9.2, 6.1 Hz, 6H), 2.67 (s, 3H), 2.17–1.95 (m, 4H). The yellow block crystals of the title compound were obtained by slow evaporation of ethanol/CHCl₂ solution (*v:v* = 2/10).

Experimental details

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

Comment

The development of efficient optoelectronic materials based on polycyclic aromatic hydrocarbons has been extensively investigated in the past decades [4–6]. Indeed, various polycyclic aromatic hydrocarbons have been used in organic light-emitting diodes (OLEDs) [7–9], organic field effect transistor (OFET) [10, 11], organic lasers [12], chemosensors [13, 14], solar cells [15] and fluorescence probes [16, 17]. Pyrene and its derivatives are important members of polycyclic aromatic hydrocarbons which have displayed several advantages such as pure blue fluorescence with high quantum yield, exceptionally long fluorescence lifetime, excellent thermal stability and high charge carrier mobility [18, 19]. However, many pyrenes tend to form excimers in solid state or in concentrated solution through π – π stacking because of the flat structure of pyrene core, resulting in a red-shifted emission, the decrease of fluorescence quantum yield and the degrade of colour purity. To suppress the aggregation and improve performance, the most effective strategies involve both the control of the supramolecular order and the optimization of functional units through the introduction of peripheral attachments into the suitable positions of pyrene. Generally, the 1-, 3-, 6- and 8-positions of pyrene core preferentially undergo electrophilic aromatic substitution reactions. Thus, various 1-substituted pyrenes, 1,6-disubstituted, 1,8-disubstituted and 1,3,6,8-tetrasubstituted pyrenes with same group can be easily obtained [18, 20–23]. There are very limited studies on 2- or 4-substituted pyrene because the position is not directly accessible by electrophilic substitution of pyrene itself, and only a few 2- or 4-substituted pyrenes have been obtained up to date [24, 25]. Recently, our group focused on the synthesis of new pyrene-based compounds with substituents on the non-active position of pyrene through indirect method via hydrogenation derivatives of pyrene [26–28]. As a continuation of our work, we synthesized one important pyrene-based compound 4-acetylpyrene using 1,2,3,6,7,8-hexahydropyrene as the starting material.

Similar to its derivative 2-acetylpyrene [28], there are two independent 4-acetylpyrene molecules in the crystal structure of the title compound. The acetyl functional group locates at the non-active 4-position of pyrene. The C–O bond length is 1.2203(14) Å for C1–O1 and 1.2211(14) Å for C19–O2 in the two 4-acetyl pyrene molecules, which is the typical double bond distance of an acetyl group. Different from its derivative 2-acetylpyrene for both independent title molecules, the methyl carbon and oxygen atoms from acetyl group are significantly deviate from the mean plane of carbon atoms of pyrene ring (see the Figure). One reason may be the space resistance of hydrogen atom at 1-position of pyrene. In one of the independent 4-acetylpyrene units, the three bond angles around the carbonyl group are 120.71(11)° for C3–C1–O1, 120.24(11)° for C2–C1–O1 and 119.02(11)° for C2–C1–C3, respectively. In the other unit, the corresponding angles are 120.50(11)° for C11–C19–O2, 120.09(11)° for C20–C19–O2 and 119.39(11)° for C21–C19–C20, respectively. The shortest distance between the adjacent pyrene planes of the two 4-acetylpyrene units is 3.362(2) and 3.390(2) Å, indicating that there are a relatively strong π – π interactions between the adjacent molecules of the title structure. The adjacent pyrene rings are almost completely parallel, forming a dimeric supramolecular structure. These dimeric supramolecular structures are linked together by relatively weak C–H... π interactions and C–H...O hydrogen bonds involving pyrene rings and carbonyl oxygen atoms, forming a three-dimensional supramolecular structure. The distances and angles of the typical bonds are similar to its derivative 2-acetylpyrene. The general supramolecular interactions is also similar to 2-acetylpyrene.

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References

1. BRUKER. SAINT, APEX2 and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Sheldrick G. M. Crystal structure refinement with Shelxl. *Acta Crystallogr.* 2015, C71, 3–8.

3. Spek A. L. Single-crystal structure validation with the program Platon. *J. Appl. Crystallogr.* 2003, **36**, 7–13.
4. Richter M. M. Electrochemiluminescence (ECL). *Chem. Rev.* 2004, **104**, 3003–3036.
5. Jacob J., Karcher W., Belliaro J. J., Wagstaffe P. J. Polycyclic aromatic compounds of environmental and occupational importance. *Fresenius Z. Anal. Chem.* 1986, **323**, 1–10.
6. Yang X., Xu X., Zhou G. Recent advances of the emitters for high performance deep-blue organic light-emitting diodes. *J. Mater. Chem. C* 2015, **3**, 913–944.
7. Farinola G. M., Ragni R. Electroluminescent materials for white organic light emitting diodes. *Chem. Soc. Rev.* 2011, **40**, 3467–3482.
8. Tao Y. T., Yang C. L., Qin J. G. Organic host materials for phosphorescent organic light-emitting diodes. *Chem. Soc. Rev.* 2011, **40**, 2943–2970.
9. Sasabe H., Kido J. J. Development of high performance OLEDs for general lighting. *J. Mater. Chem. C* 2013, **1**, 1699–1707.
10. Mei J. G., Diao Y., Appleton A. L., Fang L., Bao Z. N. Integrated materials design of organic semiconductors for field-effect transistors. *J. Am. Chem. Soc.* 2013, **135**, 6724–6746.
11. Torsi L., Magliulo M., Manoli K., Palazzo G. Organic field-effect transistor sensors: a tutorial review. *Chem. Soc. Rev.* 2013, **42**, 8612–8628.
12. Samuel I. D. W., Turnbull G. A. Organic semiconductor lasers. *Chem. Rev.* 2007, **107**, 1272–1295.
13. Wu J. S., Liu W. M., Ge J. C., Zhang H. Y., Wang P. F. New sensing mechanisms for design of fluorescent chemosensors emerging in recent years. *Chem. Soc. Rev.* 2011, **40**, 3483–3495.
14. Duke R. M., Veale E. B., Pfeffer F. M., Kruger P. E., Gunnlaugsson T. Colorimetric and fluorescent anion sensors: an overview of recent developments in the use of 1,8-naphthalimide-based chemosensors. *Chem. Soc. Rev.* 2010, **39**, 3936–3953.
15. Ouared I., Rekis M., Trari M. Phenothiazine based organic dyes for dye sensitized solar cells: a theoretical study on the role of pi-spacer. *Dyes Pigments* 2021, **190**, 109330.
16. Ni X. L., Zeng X., Redshaw C., Yamato T. Ratiometric fluorescent receptors for both Zn²⁺ and H₂PO^{−4} ions based on a pyrenyl-linked triazole-modified homooxacalix[3]arene: a potential molecular traffic signal with an R–S latch logic circuit. *J. Org. Chem.* 2011, **76**, 5696–5702.
17. Ahmed N., Shirinfar B., Geronimo I., Kim K. S. Fluorescent imidazolium-based cyclophane for detection of guanosine-5'-triphosphate and I[−] in aqueous solution of physiological pH. *Org. Lett.* 2011, **13**, 5476–5479.
18. Figueira-Duarte T. M., Mullen K. Pyrene-based materials for organic electronics. *Chem. Rev.* 2011, **111**, 7260–7314.
19. 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 Pigments* 2016, **130**, 106–115.
20. Wen B., Xu L.-H., Liu N., Ni Z.-H. Crystal structure and photochemical property of 1,8-bis(*p*-tolylthio) pyrene, C₃₀H₂₂S₂. *Z. Kristallogr. N. Cryst. Struct* 2019, **234**, 275–278.
21. Nie J., Wei J.-H., Ni Z., Synthesis H. Crystal structure and optical property of 1,6-bis(*p*-tolylthio)pyrene, C₃₀H₂₂S₂. *Z. Kristallogr. N. Cryst. Struct* 2021, **236**, 21–23.
22. 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.* 2015, **80**, 10794–10805.
23. Muangpaisal R., Ho M. C., Huang T. H., Chen C. H., Shen J. Y., Ni J. S., Lin J. T., Ke T. H., Chen L. Y., Wu C. C., Tsai C. Tetrasubstituted-pyrene derivatives for electroluminescent application. *Org. Electron.* 2014, **15**, 2148–2157.
24. Harvey R. G., Schmolka S., Cortez C., Lee H. Syntheses of 2-bromopyrene and 2-hydroxypyrene. *Synth. Commun.* 1988, **18**, 2207–2209.
25. Kreyenschmidt M., Baumgarten M., Tyutyulko N., Müllen K. 2,2'-Bipyrenyl and *para*-terpyrenyl-a new type of electronically decoupled oligoarylene. *Angew. Chem. Int. Ed.* 1994, **33**, 1957–1959.
26. Zhang R., Han F. F., Zhang L. F. Crystal structure of 2-(4-methylbenzoyl)pyrene, C₂₄H₁₆O. *Z. Kristallogr. N. Cryst. Struct* 2016, **231**, 855–857.
27. Xu Y.-H., Miao B.-X., Zhang R. Crystal structure of 2-acetyl pyrene, C₁₈H₁₂O. *Z. Kristallogr. N. Cryst. Struct* 2019, **234**, 369–371.
28. Li J.-Y., Miao B.-X., Zhao Y., Zhang L.-F. Crystal structure of 2-benzoylpyrene, C₂₃H₁₄O. *Z. Kristallogr. N. Cryst. Struct* 2020, **235**, 547–549.