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

Crystal structure of 2-benzoylpyrene, $C_{23}H_{14}O$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.10 × 0.10 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24470, 6805, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4937
$N(\text{param})_{\text{refined}}$:	433
Programs:	Bruker programs [1], SHELX [2, 3], PLATON [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.02634(10)	0.63596(12)	0.05932(5)	0.0394(3)
O2	0.39545(9)	0.65809(10)	0.16360(5)	0.0310(3)
C1	0.89505(13)	0.78178(16)	−0.03752(8)	0.0291(4)
H1	0.9443	0.8331	−0.0112	0.035*
C2	0.84704(14)	0.82490(17)	−0.09496(8)	0.0314(4)
H2	0.8628	0.9058	−0.1069	0.038*
C3	0.77541(13)	0.74734(17)	−0.13462(7)	0.0299(4)
H3	0.7444	0.7757	−0.1735	0.036*
C4	0.74977(13)	0.62796(16)	−0.11677(7)	0.0278(4)
H4	0.7021	0.5760	−0.1437	0.033*
C5	0.79525(12)	0.58588(16)	−0.05874(7)	0.0252(3)
H5	0.7760	0.5070	−0.0463	0.030*
C6	0.86977(12)	0.66146(15)	−0.01898(7)	0.0247(3)
C7	0.93111(13)	0.61109(15)	0.04071(7)	0.0264(4)
C8	0.87602(12)	0.52903(15)	0.07645(7)	0.0233(3)
C9	0.93443(12)	0.43320(15)	0.11275(7)	0.0235(3)
H9	1.0066	0.4227	0.1146	0.028*
C10	0.88560(12)	0.35307(15)	0.14632(7)	0.0221(3)
C11	0.94133(13)	0.24981(15)	0.18197(7)	0.0258(4)
H11	1.0134	0.2369	0.1841	0.031*
C12	0.89121(13)	0.17108(15)	0.21247(7)	0.0260(4)
H12	0.9294	0.1047	0.2349	0.031*
C13	0.78020(12)	0.18766(14)	0.21105(6)	0.0214(3)
C14	0.72657(14)	0.10623(15)	0.24147(7)	0.0260(4)
H14	0.7628	0.0375	0.2629	0.031*
C15	0.61980(14)	0.12638(15)	0.24019(7)	0.0280(4)
H15	0.5853	0.0711	0.2607	0.034*
C16	0.56440(13)	0.22834(15)	0.20850(7)	0.0256(3)
H16	0.4931	0.2412	0.2082	0.031*
C17	0.61464(12)	0.31231(14)	0.17699(7)	0.0213(3)
C18	0.55989(12)	0.41852(14)	0.14357(7)	0.0234(3)
H18	0.4893	0.4347	0.1438	0.028*
C19	0.60890(12)	0.49574(14)	0.11162(7)	0.0227(3)
H19	0.5712	0.5637	0.0902	0.027*
C20	0.71821(12)	0.47474(14)	0.11011(6)	0.0203(3)

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Abstract

$C_{23}H_{14}O$, monoclinic, $P2_1/c$ (no. 14), $a = 12.931(3)$ Å, $b = 10.486(2)$ Å, $c = 23.004(5)$ Å, $\beta = 104.80(3)^\circ$, $V = 3015.6(11)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0524$, $wR_{\text{ref}}(F^2) = 0.1375$, $T = 123(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C21	0.77610(12)	0.37342(13)	0.14490(6)	0.0193(3)
C22	0.72364(12)	0.29148(14)	0.17779(6)	0.0195(3)
C23	0.76917(12)	0.54962(14)	0.07546(7)	0.0226(3)
H23	0.7312	0.6141	0.0514	0.027*
C24	0.19077(13)	0.75655(16)	0.16691(7)	0.0285(4)
H24	0.1867	0.6809	0.1454	0.034*
C25	0.10214(14)	0.79999(18)	0.18448(8)	0.0358(4)
H25	0.0384	0.7544	0.1741	0.043*
C26	0.10869(15)	0.91169(17)	0.21756(8)	0.0373(4)
H26	0.0495	0.9407	0.2296	0.045*
C27	0.20314(16)	0.97979(16)	0.23253(8)	0.0360(4)
H27	0.2075	1.0540	0.2552	0.043*
C28	0.29164(14)	0.93853(15)	0.21414(7)	0.0294(4)
H28	0.3545	0.9859	0.2236	0.035*
C29	0.28599(13)	0.82559(15)	0.18135(7)	0.0235(3)
C30	0.37999(12)	0.77357(14)	0.16249(7)	0.0224(3)
C31	0.45175(12)	0.86237(14)	0.14061(7)	0.0220(3)
C32	0.55802(12)	0.82663(14)	0.14633(7)	0.0227(3)
H32	0.5843	0.7526	0.1672	0.027*
C33	0.62512(12)	0.90006(14)	0.12123(7)	0.0223(3)
C34	0.73496(13)	0.86572(15)	0.12655(7)	0.0269(4)
H34	0.7639	0.7952	0.1495	0.032*
C35	0.79679(13)	0.93451(16)	0.09866(7)	0.0295(4)
H35	0.8672	0.9096	0.1024	0.035*
C36	0.75620(13)	1.04472(15)	0.06350(7)	0.0261(4)
C37	0.81766(14)	1.11643(16)	0.03352(7)	0.0306(4)
H37	0.8878	1.0919	0.0361	0.037*
C38	0.77661(14)	1.22294(16)	0.00013(7)	0.0318(4)
H38	0.8190	1.2688	−0.0196	0.038*
C39	0.67228(14)	1.26176(15)	−0.00403(7)	0.0290(4)
H39	0.6456	1.3340	−0.0263	0.035*
C40	0.60674(13)	1.19341(14)	0.02488(7)	0.0244(3)
C41	0.49800(14)	1.22880(15)	0.02096(7)	0.0260(4)
H41	0.4700	1.3013	−0.0007	0.031*
C42	0.43494(13)	1.15951(15)	0.04796(7)	0.0246(3)
H42	0.3646	1.1847	0.0442	0.030*
C43	0.47546(12)	1.04783(14)	0.08230(6)	0.0208(3)
C44	0.58303(12)	1.01110(14)	0.08764(6)	0.0214(3)
C45	0.64898(13)	1.08363(14)	0.05884(7)	0.0228(3)
C46	0.41177(12)	0.97325(14)	0.10963(7)	0.0225(3)
H46	0.3417	0.9980	0.1071	0.027*

Source of material

The title compound 2-benzoylpyrene was obtained by two steps using 4,5,9,10-tetrahydroxyphenylene as the starting materials. The educt 4,5,9,10-tetrahydroxyphenylene was prepared according to the previous literature [5]. The whole synthetic procedures were referred to the method reported recently by Zhang et al. [6]. The detailed synthetic processes are described as following. 4,5,9,10-tetrahydroxyphenylene (7 mmol) was dissolved in carbon disulfide (100 mL) and then anhydrous aluminum chloride (14 mmol) was added under nitrogen atmosphere. The mixture was kept below 0 °C and

stirred for 30 min. Then it was added dropwise into a solution of benzoyl chloride (74 mmol) in carbon disulfide (20 mL), and the mixture was stirred at room temperature for 10 h. After the reaction completed, the mixture was poured into 150 mL ice water and stirred overnight. The mixture was extracted with dichloromethane three times and the collected organic layer was combined, washed with brine twice and dried over anhydrous magnesium sulfate. The crude product was condensed and purified on a silica-gel column using a mixture of dichloromethane and hexane as eluent, yielding the intermediate 2-benzoyl-4,5,9,10-tetrahydroxyphenylene as a yellow needle-like crystal (Yield: 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.90–7.82 (m, 2H), 7.62 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.54 (dd, *J* = 15.2, 7.4 Hz, 4H), 7.22 (dd, *J* = 8.2, 6.6 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 2.96 (s, 8H). MS: (C₂₃H₁₈O) *m/z* 310(M⁺, 100), 233(58), 202(30), 105(32).

The preparative method of the title compound as follows. A solution of 2-benzoyl-4,5,9,10-tetrahydroxyphenylene (5 mmol) and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzochinone, 11 mmol) in dry toluene (50 mL) were heated at reflux under nitrogen atmosphere for 24 h. The mixture was cooled to room temperature and filtered. The filtrate was washed with 5% aqueous sodium hydroxide and water and dried over anhydrous magnesium sulfate. The crude product was purified on a silica-gel column using a mixture of dichloromethane and hexane as eluent, yielding light yellow block-like crystals (Yield: 73%). A suitable block single crystal of the compound for X-ray crystallography was obtained by the slow evaporation of a mixture of dichloromethane/hexane at room temperature. ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 2H), 8.25 (d, *J* = 7.7 Hz, 2H), 8.15 (s, 4H), 8.10 (t, *J* = 7.6 Hz, 1H), 8.01–7.94 (m, 2H), 7.73 (s, 1H), 7.59 (t, *J* = 7.6 Hz, 2H). MS: (C₂₃H₁₄O) *m/z* 306(M⁺, 100), 229(25), 201(60), 105(20), 77(28).

Experimental details

All H atoms were introduced using the HFIX command in the SHELXL program [3], with the value of 0.93 Å for C–H bonds distances. All H atoms were allowed for as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ for all hydrogen atoms. The structure was checked using PLATON [4].

Comment

Organic optoelectronic materials such as organic light emitting diodes (OLEDs), organic photovoltaic cells (OPV), organic field-effect transistors (OFETs), fluorescent probe, etc. [7], have aroused much attentions in several fields. Up to date, there are several tens of important functional precursors for the design, synthesis of interesting new organic optoelectronic materials [8]. As one of the well-known starting functional material, new pyrene-based organic functional compounds have been paid everlasting attentions due to

not only their excellent photophysical properties, but also their precursor pyrene easily obtained from coal tar as the huge side product of coal coking. For example, the pyrene-based derivatives OLED have been wide application and broad prospects, because some pyrene-based derivatives are easier to make thinner, lighter, flexible and large-area sheets [9, 10]. In addition, pyrene-based derivatives also have been widely employed in fluorescent probes with low detection limit and high sensitivity characteristics due to pyrene-based fluorescent probes usually exhibit high solution fluorescence quantum yield and large Stokes shift [11, 12]. But most of the reported pyrene-based derivatives are 1-monosubstituted compounds and 1,3,6,8-tetrasubstituted compounds because 1-, 3-, 6-, 8-positions are commonly active sites of pyrene for nucleophilic substitution reaction. The research on inactive sites such as 2-, 7-position of pyrene recently arouse the interest of scientists [13], which can bring new pyrene-based functional materials with interesting optoelectronic properties. It is very hard to directly obtain 2-, 7-position substituted and pyrene-based derivatives from pyrene, therefore, the 2-substituted and 2,7-disubstituted pyrene-based derivatives are still very limited. Zhang et al. [6, 10] have reported the synthesis and crystal structure of one benzoylpyrene with 4-methylbenzoyl group at the 2-position of pyrene *via* three steps using pyrene as the starting material.

The single crystal X-ray diffraction analysis results are consistent with expectation. There are two independent 2-benzoylpyrene molecules in the crystal structure. The crystal structure indicates that the benzoyl group is bonded to the 2-position of the pyrene precursor. The functional group C=O bond length is 1.2241(19) Å for C7–O1 and 1.2265(18) Å for C30–O2 in the two 2-benzoylpyrene molecules, respectively, which conforms to the typical characteristics of the carbonyl C=O double bond. The bond angles around the carbonyl group in the two independent 2-benzoylpyrene molecules are 119.73(15)° for C6–C7–O1 and 119.65(14)° for O2–C30–C29. All the sixteen carbon atoms of pyrene moiety are located on a nearly strict plane with the largest derivation of 0.073(2) Å for C8 and 0.063(2) Å for C31 from the mean plane. The dihedral angle between the pyrene ring and the phenyl moieties are 65.43(15)° and 65.51(15)° in the two molecules, respectively. All molecular geometric parameters of both crystallographically independent are in the expected ranges [14]. There are many interactions in the crystal of the title compound. Firstly, there exist strong π - π interactions between the neighboring pyrene rings with the shortest C–C distance of 3.382 Å, forming dimeric supramolecular substructures. Then, these dimeric substructures are linked together by C–H $\cdots$ O hydrogen bonds, giving a one-dimensional zigzag-like supramolecular structure. Finally, a three-dimensional network supramolecular structure is obtained based on the

above one-dimensional zigzag-like supramolecular structures linked by C–H- π interactions from the adjacent pyrene rings and benzene rings.

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References

1. Bruker: APEX3, SAINT-Plus, XPREP. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7–13.
5. Tintel, C.; Rietmeyer, F. J.; Cornelisse, J.: Photosubstitution and photoreduction of pyrene and 1-halopyrenes. *Rec. Trav. Chim. Pays Bas* **102** (1983) 224–228.
6. Zhang, R.; Han, F. F.; Zhang, L. F.: Crystal structure of 2-(4-methylbenzoyl)pyrene, C₂₄H₁₆O. *Z. Kristallogr. NCS* **231** (2016) 855–857.
7. Sun, H.; Tang, X. X.; Miao, B. X.; Yang, Y.; Ni, Z. H.: A new AIE and TICT-active tetraphenylethene-based thiazole compound: Synthesis, structure, photophysical properties and application for water detection in organic solvents. *Sensor Actuat. B-Chem.* **267** (2018) 448–456.
8. Sun, H.; Sun, S. S.; Han, F. F.; Ni, Z. H.; Zhang, R.; Li, M. D.: A new tetraphenylethene-based Schiff base: two crystalline polymorphs exhibiting totally different photochromic and fluorescence properties. *J. Mater. Chem. C* **7** (2019) 7053–7060.
9. Figueira-Duarte, T. M.; Müllen, K.: Pyrene-based materials for organic electronics. *Chem. Rev.* **111** (2011) 7260–7314.
10. Zhang, R.; Zhao, Y.; Zhang, T. 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.
11. Tang, X. X.; Sun, H.; Nie, J.; Han, X. E.; Zhao, Y.; Zhang, R.; Ni, Z. H.: An o-hydroxyl aldehyde structure based naphthalimide derivative: Reversible photochromic properties and its application in ClO[−] detection in living cells. *Spectrochim. Acta A* **219** (2019) 154–163.
12. Nie, J.; Liu, Y.; Niu, J.; Ni, Z. H.; Lin, W. Y.: A new pyrene-based fluorescent probe with large Stokes shift for detecting hydrogen peroxide in aqueous solution and living cells. *J. Photoch. Photobiol. A* **348** (2017) 1–7.
13. Ji, L.; Edkins, R. M.; Lorbach, A.; Krummenacher, I.; Brückner, C.; Eichhorn, A.; Braunschweig, H.; Engels, B.; Low, P. J.; Marder, T. B.: Electron delocalization in reduced forms of 2-(BMes₂)pyrene and 2,7-bis(BMes₂)pyrene. *J. Am. Chem. Soc.* **137** (2015) 6750–6753.
14. Xu, Y.-H.; Miao, B.-X.; Zhang, R.: Crystal structure of 2-acetylpyrene, C₁₈H₁₂O. *Z. Kristallogr. NCS* **234** (2019) 369–371.