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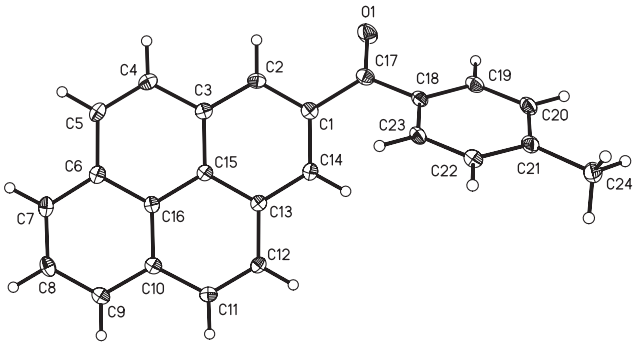
Crystal structure of 2-(4-methylbenzoyl)pyrene, $C_{24}H_{16}O$



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Abstract

$C_{24}H_{16}O$, monoclinic, $P2_1/c$ (no. 14), $a = 13.642(3)$ Å, $b = 10.787(2)$ Å, $c = 11.551(2)$ Å, $\beta = 110.73(3)°$, $V = 1589.8(6)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0506$, $wR_{ref}(F^2) = 0.1482$, $T = 293(2)$ K.

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Tables 1–3 contain details of the methods used and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

4,5,9,10-Tetrahydrogenpyrene was prepared according to the reported synthetic protocol [1].

A solution of 2-(4-methylbenzoyl)-4,5,9,10-tetrahydr opyrene (5.0 mmol) and (2,3-dichloro-5,6-dicyano-1,4-benzochinone) (11.0 mmol) in dry toluene (80 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, yielding yellow plate crystals (yield: 74%). Crystals were obtained by the slow evaporation of a mixture of dichloromethane/hexane at room temperature. Elemental analysis: Calculated for $C_{24}H_{16}O$: C, 89.97%; H, 5.03%; O, 4.99%; found: C, 89.88%, H, 5.01%; O, 5.05%.

Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.06×0.08×0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.80 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω scans
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13561, 3121
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2831
$N(param)_{refined}$:	227
Programs:	SHELX [2], Platon [3]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4e	0.3756	−0.1380	0.3846	0.030
H(4)	4e	0.3191	−0.3138	0.2328	0.033
H(5)	4e	0.1935	−0.4079	0.0743	0.033
H(7)	4e	0.0087	−0.4140	−0.0781	0.032
H(8)	4e	−0.1573	−0.3311	−0.1542	0.032
H(9)	4e	−0.1980	−0.1536	−0.0688	0.031
H(11)	4e	−0.1422	0.0200	0.0855	0.027
H(12)	4e	−0.0149	0.1188	0.2391	0.027
H(14)	4e	0.1718	0.1326	0.3803	0.027
H(19)	4e	0.4447	0.2157	0.6967	0.032
H(20)	4e	0.4489	0.4286	0.7125	0.035
H(22)	4e	0.3207	0.4561	0.3430	0.031
H(23)	4e	0.3123	0.2432	0.3271	0.029
H(24A)	4e	0.4058	0.6290	0.6245	0.052
H(24B)	4e	0.3138	0.6360	0.4963	0.052
H(24C)	4e	0.4304	0.6392	0.5021	0.052

Experimental details

All H atoms were introduced using the HFIX option in the SHELXL program [2], with the value of 0.93 Å or 0.96 Å

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Table 3: Fractional coordinates and atomic displacement parameters (Å²).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.2865(1)	0.0076(1)	0.3971(1)	0.0258(8)	0.0234(8)	0.0215(8)	−0.0014(6)	0.0082(7)	0.0039(6)
C(2)	4*e*	0.3087(1)	−0.1042(2)	0.3511(2)	0.0225(8)	0.0252(8)	0.0253(8)	0.0031(6)	0.0069(6)	0.0055(6)
C(3)	4*e*	0.2316(1)	−0.1661(1)	0.2552(1)	0.0243(8)	0.0223(8)	0.0235(8)	0.0005(6)	0.0102(6)	0.0037(6)
C(4)	4*e*	0.2525(1)	−0.2791(2)	0.2017(2)	0.0273(8)	0.0245(8)	0.0315(9)	0.0044(7)	0.0121(7)	0.0035(7)
C(5)	4*e*	0.1773(1)	−0.3355(2)	0.1073(2)	0.0340(9)	0.0205(8)	0.0315(9)	0.0020(7)	0.0169(7)	−0.0014(7)
C(6)	4*e*	0.0727(1)	−0.2866(1)	0.0564(1)	0.0288(8)	0.0215(8)	0.0226(8)	−0.0010(6)	0.0125(7)	0.0022(6)
C(7)	4*e*	−0.0061(1)	−0.3424(2)	−0.0426(2)	0.0367(9)	0.0224(8)	0.0235(8)	−0.0037(7)	0.0138(7)	−0.0028(6)
C(8)	4*e*	−0.1060(1)	−0.2926(2)	−0.0884(2)	0.0307(8)	0.0282(9)	0.0215(8)	−0.0092(7)	0.0081(7)	−0.0015(7)
C(9)	4*e*	−0.1304(1)	−0.1857(2)	−0.0372(2)	0.0236(8)	0.0292(9)	0.0234(8)	−0.0022(6)	0.0076(6)	0.0036(7)
C(10)	4*e*	−0.0539(1)	−0.1258(2)	0.0616(1)	0.0240(8)	0.0237(8)	0.0204(8)	−0.0015(6)	0.0096(6)	0.0042(6)
C(11)	4*e*	−0.0750(1)	−0.0132(2)	0.1149(1)	0.0209(7)	0.0250(8)	0.0242(8)	0.0011(6)	0.0100(6)	0.0042(6)
C(12)	4*e*	0.0009(1)	0.0456(1)	0.2069(1)	0.0251(8)	0.0208(8)	0.0233(8)	0.0014(6)	0.0112(6)	0.0004(6)
C(13)	4*e*	0.1057(1)	−0.0029(1)	0.2560(1)	0.0236(8)	0.0208(7)	0.0197(8)	0.0002(6)	0.0107(6)	0.0032(6)
C(14)	4*e*	0.1858(1)	0.0577(1)	0.3494(1)	0.0279(8)	0.0199(7)	0.0201(8)	−0.0010(6)	0.0101(6)	0.0007(6)
C(15)	4*e*	0.1288(1)	−0.1155(1)	0.2073(1)	0.0231(8)	0.0199(7)	0.0185(7)	−0.0006(6)	0.0099(6)	0.0033(6)
C(16)	4*e*	0.0488(1)	−0.1763(1)	0.1088(1)	0.0242(8)	0.0210(8)	0.0181(7)	−0.0025(6)	0.0094(6)	0.0019(6)
C(17)	4*e*	0.3697(1)	0.0675(2)	0.5039(1)	0.0247(8)	0.0316(9)	0.0209(8)	0.0004(7)	0.0063(7)	0.0029(7)
C(18)	4*e*	0.3754(1)	0.2060(2)	0.5103(1)	0.0177(7)	0.0285(8)	0.0222(8)	−0.0025(6)	0.0053(6)	−0.0028(6)
C(19)	4*e*	0.4181(1)	0.2637(2)	0.6255(2)	0.0217(8)	0.0370(9)	0.0196(8)	−0.0005(7)	0.0040(6)	−0.0011(7)
C(20)	4*e*	0.4212(1)	0.3916(2)	0.6350(2)	0.0216(8)	0.041(1)	0.0236(8)	−0.0032(7)	0.0055(6)	−0.0108(7)
C(21)	4*e*	0.3833(1)	0.4657(2)	0.5296(2)	0.0179(7)	0.0319(9)	0.0321(9)	−0.0037(6)	0.0103(6)	−0.0078(7)
C(22)	4*e*	0.3441(1)	0.4080(2)	0.4144(2)	0.0228(8)	0.0292(9)	0.0241(8)	−0.0018(6)	0.0072(6)	0.0008(7)
C(23)	4*e*	0.3395(1)	0.2801(2)	0.4047(1)	0.0207(7)	0.0302(9)	0.0188(8)	−0.0038(6)	0.0050(6)	−0.0039(6)
C(24)	4*e*	0.3834(1)	0.6052(2)	0.5390(2)	0.0277(9)	0.033(1)	0.042(1)	−0.0031(7)	0.0123(8)	−0.0108(8)
O(1)	4*e*	0.4303(1)	0.0042(1)	0.5858(1)	0.0396(7)	0.0362(7)	0.0283(7)	0.0021(6)	−0.0033(6)	0.0053(5)

for C—H bonds distances. All H atoms were allowed for as riding atoms with $U_{iso}(H) = 1.5U_{eq}$(methyl carrier) and $U_{iso}(H) = 1.2U_{eq}(C)$ for all other hydrogen atoms. The structure was checked using PLATON [3].

Discussion

As one of the most known polycyclic aromatic hydrocarbons, pyrene has been extensively studied as fluorophore because of its pure blue fluorescence with high quantum yield, long fluorescence lifetime, excellent thermal stability and high charge carrier mobility. In recent years, many functionalized pyrenes have been investigated and utilized as excellent materials for organic solar cells (OSCs), organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), etc [4, 5]. However, the reported pyrene derivatives are almost 1-, or 1-, 3-, 6-, and 8-substituted pyrene-based compounds [6–8]. The synthesis of 2-substituted pyrene derivatives is synthetically challenging due to the presence of the nodal plane in the HOMO and LUMO, which lies perpendicular to the molecule and passes through the 2-position [9, 10]. Up to date, there are only a few reports on 2-substituted pyrene-based compounds especially their crystal structures.

There is one molecule in the asymmetric unit of the title structure which is shown in the figure. The 4-methylbenzoyl group is attached to the 2-position of the pyrenyl core. The C—O bond distance is 1.2208(19) Å for C17—O1, which is normal for diarylketones. The three bond angles around the carbonyl group are 118.90(13)° for C1—C17—C18, 120.39(15)° for C1—C17—O1 and 120.69(15)° for C18—C17—O1, respectively. All carbon atoms of pyrene ring locate on a plane with the largest derivation of 0.053(2) Å for C14 atom from the mean plane. The dihedral angel between the pyrene ring and benzene ring is 55.61(15)°. Molecules are linked by C—H···O hydrogen bonds to form one-dimensional zizag chain-like supramolecular structure. These chains are linked by π–π and C—H–π interactions, giving a three-dimensional network.

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