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2,3:6,7-Bis(methylenedioxy)-phenanthrene

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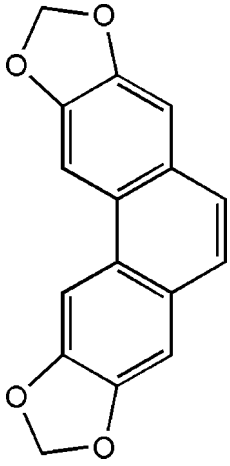
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.045; wR factor = 0.126; data-to-parameter ratio = 11.7.

In the title molecule, $C_{16}H_{10}O_4$, all the non-H atoms are coplanar. The crystal structure is stabilized by weak intermolecular C—H···O contacts and π–π stacking interactions (the interplanar distance is 3.43 Å).

Related literature

For related literature, see: Cragg *et al.* (1982); Nordlander & Njoroge (1987); Pausacker (1953); Wang *et al.* (2007).



Experimental

Crystal data

$C_{16}H_{10}O_4$
M_r = 266.24
Triclinic, $P\overline{1}$
a = 6.862 (2) Å
b = 7.775 (2) Å
c = 11.495 (3) Å
α = 75.084 (3)°
β = 77.118 (3)°
γ = 86.460 (4)°
V = 577.7 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 293 (2) K
0.34 × 0.30 × 0.25 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.963, T_{max} = 0.973
4267 measured reflections
2126 independent reflections
1543 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.126
S = 1.04
2126 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O1^{i}	0.93	2.69	3.442 (3)	139

Symmetry code: (i) $-x+2, -y, -z+1$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HJ2009).

References

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supporting information

Acta Cryst. (2008). E**64**, o276 [https://doi.org/10.1107/S1600536807065592]

2,3:6,7-Bis(methylenedioxy)phenanthrene

Yuan-Xing Wang, Chong-Bo Liu, Zhi-Jie Fang, Ming-Yong Xie and Xiao-Bo Hu

S1. Comment

Recently, our group (Wang *et al.*, 2007) decribed the crystal structure of 2,3-Dimethoxy-6,7- methylenedioxy-phenanthrene [1] (C17H14O4). Here we report the crystal structure of 2,3:6,7-bis(methylenedioxy)phenanthrene, another important intermediate in the synthesis of phenanthroindolizidine and phenanthroquinolizidine alkaloids analogs. In the title molecule, all the non-hydrogen atoms are nearly coplanar, with the mean deviation of 0.0763 Å, The crystal structure is stabilized by weak intermolecular C11—H11···O1 contacts with C···O distance 3.442 (3) Å and π–π stacking interactions between the parallel molecules; the interplanar distance is 3.43 Å (symmetry code: -1 + *x*, *y*, *z*).

S2. Experimental

The title compound was synthesized by the route depicted in Fig. 2 [Pausacker, 1953; Cragg *et al.*, 1982; Nordlander & Njoroge, 1987] and recrystallized from chloroform–anhydrous ethanol (1:3, *v*/*v*) to give 2.2 g (50.3%) of block yellow crystals.

S3. Refinement

All H atoms were positioned geometrically and treated as riding (C—H = 0.97 Å for methylene and C—H = 0.93 Å for phenyl). U_{iso}(H) = 1.5 for methyl and 1.2 U_{eq}(C) for others of the carrier atom.

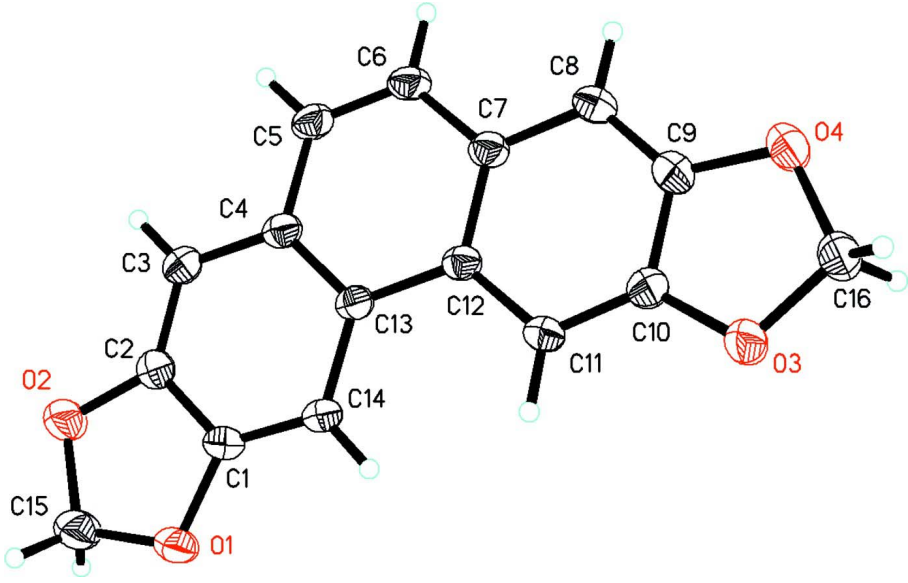

Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

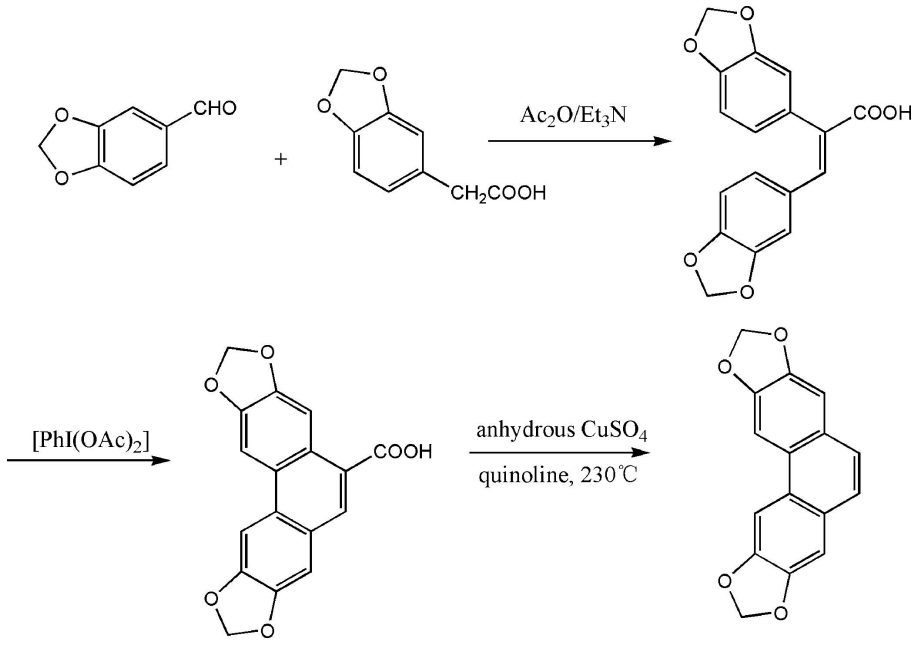

Figure 2

Synthesis of the title compound.

2,3:6,7-Bis(methylenedioxy)phenanthrene

Crystal data

$C_{16}H_{10}O_4$
$M_r = 266.24$
Triclinic, $P\overline{1}$
Hall symbol: -p 1
$a = 6.862$ (2) Å
$b = 7.775$ (2) Å
$c = 11.495$ (3) Å
$\alpha = 75.084$ (3)°
$\beta = 77.118$ (3)°
$\gamma = 86.460$ (4)°
$V = 577.7$ (3) Å^3
$Z = 2$
$F(000) = 276$
$D_x = 1.531$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1555 reflections
$\theta = 2.7$–$28.2°$
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Block, yellow
0.34 × 0.30 × 0.25 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.963$, $T_{max} = 0.973$
4267 measured reflections
2126 independent reflections
1543 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.7°$
$h = -8\rightarrow7$
$k = -9\rightarrow9$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.126$
$S = 1.04$
2126 reflections
181 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.0394P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.98631 (17)	0.29142 (18)	0.28720 (11)	0.0600 (4)
O2	0.76359 (19)	0.46464 (18)	0.18194 (11)	0.0593 (4)
O3	0.60609 (18)	−0.23746 (17)	0.93565 (11)	0.0600 (4)
O4	0.27411 (19)	−0.20727 (18)	1.02816 (11)	0.0635 (4)
C1	0.7991 (2)	0.2792 (2)	0.36405 (16)	0.0419 (4)
C2	0.6664 (2)	0.3858 (2)	0.30069 (15)	0.0431 (4)
C3	0.4708 (2)	0.3990 (2)	0.35505 (15)	0.0440 (4)
H3	0.3823	0.4701	0.3126	0.053*
C4	0.4065 (2)	0.3002 (2)	0.47905 (15)	0.0386 (4)
C5	0.2024 (2)	0.3094 (2)	0.53970 (16)	0.0455 (4)
H5	0.1136	0.3796	0.4970	0.055*
C6	0.1352 (2)	0.2188 (2)	0.65725 (16)	0.0461 (4)
H6	0.0013	0.2291	0.6942	0.055*
C7	0.2640 (2)	0.1071 (2)	0.72689 (15)	0.0399 (4)
C8	0.1875 (3)	0.0104 (2)	0.84929 (16)	0.0481 (5)
H8	0.0540	0.0210	0.8869	0.058*
C9	0.3135 (3)	−0.0980 (2)	0.91036 (16)	0.0459 (4)
C10	0.5148 (2)	−0.1147 (2)	0.85469 (16)	0.0424 (4)
C11	0.5953 (2)	−0.0243 (2)	0.73845 (14)	0.0398 (4)
H11	0.7298	−0.0374	0.7040	0.048*
C12	0.4690 (2)	0.0916 (2)	0.66999 (14)	0.0359 (4)
C13	0.5411 (2)	0.1911 (2)	0.54379 (14)	0.0356 (4)
C14	0.7449 (2)	0.1829 (2)	0.48162 (15)	0.0403 (4)
H14	0.8375	0.1130	0.5211	0.048*
C15	0.9666 (3)	0.4100 (3)	0.17378 (17)	0.0599 (5)
H15A	1.0083	0.3512	0.1073	0.072*
H15B	1.0511	0.5130	0.1564	0.072*
C16	0.4614 (3)	−0.2862 (2)	1.04828 (16)	0.0522 (5)
H16A	0.5025	−0.2446	1.1118	0.063*

H16B	0.4489	−0.4147	1.0753	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0334 (7)	0.0854 (9)	0.0466 (8)	0.0035 (6)	0.0006 (5)	0.0004 (7)
O2	0.0483 (8)	0.0723 (9)	0.0444 (8)	0.0037 (6)	−0.0038 (6)	0.0023 (6)
O3	0.0475 (8)	0.0713 (9)	0.0447 (8)	0.0138 (6)	−0.0030 (6)	0.0055 (6)
O4	0.0509 (8)	0.0801 (9)	0.0424 (8)	0.0079 (7)	0.0017 (6)	0.0029 (7)
C1	0.0294 (8)	0.0502 (10)	0.0448 (10)	−0.0010 (7)	−0.0045 (7)	−0.0120 (8)
C2	0.0419 (10)	0.0460 (10)	0.0395 (10)	−0.0014 (7)	−0.0081 (8)	−0.0073 (8)
C3	0.0399 (10)	0.0484 (10)	0.0439 (10)	0.0062 (7)	−0.0146 (8)	−0.0085 (8)
C4	0.0327 (9)	0.0420 (9)	0.0442 (10)	0.0031 (7)	−0.0102 (7)	−0.0154 (7)
C5	0.0340 (9)	0.0530 (10)	0.0517 (11)	0.0112 (7)	−0.0147 (8)	−0.0149 (8)
C6	0.0283 (8)	0.0606 (11)	0.0507 (11)	0.0081 (8)	−0.0058 (7)	−0.0204 (9)
C7	0.0326 (9)	0.0474 (9)	0.0413 (10)	0.0030 (7)	−0.0061 (7)	−0.0165 (7)
C8	0.0333 (9)	0.0626 (11)	0.0445 (10)	0.0037 (8)	0.0007 (7)	−0.0153 (9)
C9	0.0431 (10)	0.0518 (10)	0.0402 (10)	0.0001 (8)	−0.0028 (7)	−0.0121 (8)
C10	0.0397 (9)	0.0443 (9)	0.0420 (10)	0.0051 (7)	−0.0098 (7)	−0.0088 (7)
C11	0.0305 (8)	0.0465 (9)	0.0397 (9)	0.0033 (7)	−0.0026 (7)	−0.0110 (7)
C12	0.0310 (8)	0.0390 (8)	0.0403 (9)	0.0019 (7)	−0.0074 (7)	−0.0152 (7)
C13	0.0308 (8)	0.0389 (9)	0.0398 (9)	0.0013 (7)	−0.0093 (7)	−0.0135 (7)
C14	0.0286 (8)	0.0483 (10)	0.0433 (10)	0.0031 (7)	−0.0092 (7)	−0.0094 (8)
C15	0.0429 (11)	0.0717 (13)	0.0524 (12)	−0.0024 (9)	−0.0011 (9)	−0.0005 (10)
C16	0.0535 (11)	0.0535 (11)	0.0422 (10)	0.0043 (8)	−0.0037 (8)	−0.0059 (8)

Geometric parameters (Å, º)

O1—C1	1.3804 (19)	C6—C7	1.428 (2)
O1—C15	1.419 (2)	C6—H6	0.9300
O2—C2	1.3776 (19)	C7—C8	1.413 (2)
O2—C15	1.421 (2)	C7—C12	1.425 (2)
O3—C10	1.378 (2)	C8—C9	1.352 (2)
O3—C16	1.423 (2)	C8—H8	0.9300
O4—C9	1.379 (2)	C9—C10	1.400 (2)
O4—C16	1.430 (2)	C10—C11	1.349 (2)
C1—C14	1.347 (2)	C11—C12	1.423 (2)
C1—C2	1.392 (2)	C11—H11	0.9300
C2—C3	1.358 (2)	C12—C13	1.448 (2)
C3—C4	1.419 (2)	C13—C14	1.427 (2)
C3—H3	0.9300	C14—H14	0.9300
C4—C13	1.418 (2)	C15—H15A	0.9700
C4—C5	1.425 (2)	C15—H15B	0.9700
C5—C6	1.344 (2)	C16—H16A	0.9700
C5—H5	0.9300	C16—H16B	0.9700
C1—O1—C15	106.30 (13)	C8—C9—C10	121.33 (17)
C2—O2—C15	105.66 (13)	O4—C9—C10	109.68 (15)

C10—O3—C16	106.44 (13)	C11—C10—O3	128.20 (15)
C9—O4—C16	105.87 (13)	C11—C10—C9	122.71 (16)
C14—C1—O1	127.84 (15)	O3—C10—C9	109.07 (15)
C14—C1—C2	123.24 (15)	C10—C11—C12	118.25 (15)
O1—C1—C2	108.91 (15)	C10—C11—H11	120.9
C3—C2—O2	128.62 (16)	C12—C11—H11	120.9
C3—C2—C1	121.32 (16)	C11—C12—C7	118.78 (15)
O2—C2—C1	110.05 (14)	C11—C12—C13	122.16 (14)
C2—C3—C4	117.53 (16)	C7—C12—C13	119.06 (15)
C2—C3—H3	121.2	C4—C13—C14	118.50 (15)
C4—C3—H3	121.2	C4—C13—C12	119.54 (14)
C13—C4—C3	121.32 (15)	C14—C13—C12	121.96 (14)
C13—C4—C5	119.18 (15)	C1—C14—C13	118.09 (15)
C3—C4—C5	119.50 (15)	C1—C14—H14	121.0
C6—C5—C4	121.52 (16)	C13—C14—H14	121.0
C6—C5—H5	119.2	O1—C15—O2	109.01 (14)
C4—C5—H5	119.2	O1—C15—H15A	109.9
C5—C6—C7	121.71 (15)	O2—C15—H15A	109.9
C5—C6—H6	119.1	O1—C15—H15B	109.9
C7—C6—H6	119.1	O2—C15—H15B	109.9
C8—C7—C12	120.73 (15)	H15A—C15—H15B	108.3
C8—C7—C6	120.27 (15)	O3—C16—O4	108.43 (14)
C12—C7—C6	118.99 (15)	O3—C16—H16A	110.0
C9—C8—C7	118.20 (16)	O4—C16—H16A	110.0
C9—C8—H8	120.9	O3—C16—H16B	110.0
C7—C8—H8	120.9	O4—C16—H16B	110.0
C8—C9—O4	128.98 (16)	H16A—C16—H16B	108.4

C15—O1—C1—C14	−179.56 (17)	C8—C9—C10—O3	−177.95 (16)
C15—O1—C1—C2	0.33 (19)	O4—C9—C10—O3	1.0 (2)
C15—O2—C2—C3	178.81 (18)	O3—C10—C11—C12	177.57 (15)
C15—O2—C2—C1	−2.50 (19)	C9—C10—C11—C12	−0.4 (3)
C14—C1—C2—C3	0.1 (3)	C10—C11—C12—C7	0.0 (2)
O1—C1—C2—C3	−179.80 (14)	C10—C11—C12—C13	−178.68 (14)
C14—C1—C2—O2	−178.70 (15)	C8—C7—C12—C11	0.5 (2)
O1—C1—C2—O2	1.40 (19)	C6—C7—C12—C11	−178.00 (14)
O2—C2—C3—C4	178.62 (15)	C8—C7—C12—C13	179.20 (14)
C1—C2—C3—C4	0.1 (2)	C6—C7—C12—C13	0.7 (2)
C2—C3—C4—C13	−0.2 (2)	C3—C4—C13—C14	0.3 (2)
C2—C3—C4—C5	−179.74 (14)	C5—C4—C13—C14	179.76 (13)
C13—C4—C5—C6	0.8 (2)	C3—C4—C13—C12	−179.58 (14)
C3—C4—C5—C6	−179.66 (16)	C5—C4—C13—C12	−0.1 (2)
C4—C5—C6—C7	−0.8 (3)	C11—C12—C13—C4	178.00 (14)
C5—C6—C7—C8	−178.48 (16)	C7—C12—C13—C4	−0.7 (2)
C5—C6—C7—C12	0.0 (2)	C11—C12—C13—C14	−1.8 (2)
C12—C7—C8—C9	−0.5 (3)	C7—C12—C13—C14	179.49 (13)
C6—C7—C8—C9	177.93 (16)	O1—C1—C14—C13	179.80 (15)
C7—C8—C9—O4	−178.66 (16)	C2—C1—C14—C13	−0.1 (3)

C7—C8—C9—C10	0.1 (3)	C4—C13—C14—C1	−0.1 (2)
C16—O4—C9—C8	−177.63 (18)	C12—C13—C14—C1	179.74 (14)
C16—O4—C9—C10	3.49 (19)	C1—O1—C15—O2	−1.9 (2)
C16—O3—C10—C11	176.67 (17)	C2—O2—C15—O1	2.7 (2)
C16—O3—C10—C9	−5.13 (19)	C10—O3—C16—O4	7.28 (19)
C8—C9—C10—C11	0.4 (3)	C9—O4—C16—O3	−6.63 (19)
O4—C9—C10—C11	179.36 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O1^{i}	0.93	2.69	3.442 (3)	139

Symmetry code: (i) −*x*+2, −*y*, −*z*+1.