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2,3-Dimethoxy-6,7-methylenedioxyphenanthrene

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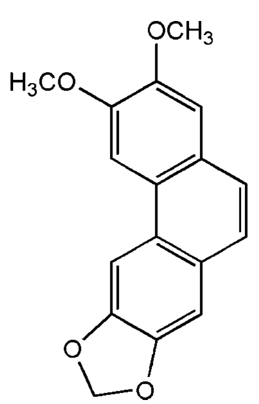
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.096; data-to-parameter ratio = 12.7.

In the title molecule, $C_{17}H_{14}O_4$, all non-H atoms are essentially coplanar. The crystal structure is stabilized by weak intermolecular C—H···O hydrogen bonds.

Related literature

For related literature, see: Cragg *et al.* (1982); Gao *et al.* (2004); Gellert (1982); Nordlander & Njoroge (1987); Pausacker (1953); Ratnagiriswaran & Venkatachalam (1935); Staerk *et al.* (2000); Wu *et al.* (2002).



Experimental

Crystal data

$C_{17}H_{14}O_4$
M_r = 282.28
Monoclinic, $P2_1/c$
a = 7.370 (2) Å
b = 18.375 (5) Å
c = 9.840 (3) Å
β = 96.363 (4)°
V = 1324.3 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.20 × 0.15 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.980, T_{max} = 0.994
8248 measured reflections
2452 independent reflections
1011 reflections with $I > 2\sigma(I)$
R_{int} = 0.078

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.096
S = 1.03
2452 reflections
193 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C17—H17B···O3^i	0.96	2.51	3.465 (3)	174

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

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: LH2479).

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supplementary materials

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2,3-Dimethoxy-6,7-methylenedioxyphenanthrene

Y.-X. Wang, C.-B. Liu, Z.-J. Fang, H.-L. Wen and M.-Y. Xie

Comment

Phenanthroindolizidine alkaloids are extensively present in various plants of the Asclepiadaceae family (Gellert, 1982; Staerk *et al.*, 2000). These natural products exhibit interesting biological properties, such as emetic and vesicant properties, unusual cardiovascular and immunological efects, nerve growth stimulation and probable anti-inflammatory, especially anti-tumor activity. Since the first isolation of (-)-tylophorine in 1935 (Ratnagiriswaran & Venkatachalam, 1935), phenanthroindolizidine alkaloids have engendered a great deal of synthetic work. To further evaluate the antitumor potential of these analogs (Gao *et al.*, 2004; Wu *et al.*, 2002), we plan to synthesize some tylophorine analogs that have a mode of action different from known antitumor drugs. 2,3-Dimethoxy-6,7-methylenedioxyphenanthrene is an important intermediate in the synthesis of phenanthroindolizidine alkaloid analogs. Here we report the synthesis and structure of the title compound. In the title molecule all non-hydrogen atoms are essentially coplanar, with the mean deviation of 0.0432 Å. The crystal structure is stabilized by weak intermolecular C—H···O hydrogen bonds.

Experimental

The title compound was synthesized by the route depicted in Fig. 3 (Pausacker, 1953; Cragg *et al.*, 1982, Nordlander & Njoroge, 1987) and recrystallized from chloroform–anhydrous ethanol (1:3, *v*/*v*) to give 1.5 g (56.4%) of block-shaped light yellow crystals.

Refinement

All H atoms were positioned geometrically and treated as riding (C—H = 0.96 Å for methyl; C—H = 0.93 Å for phenyl and C—H = 0.97 Å for methylene). U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for methyl H atoms.

Figures

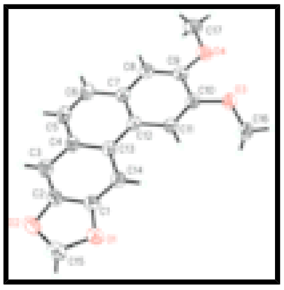


Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

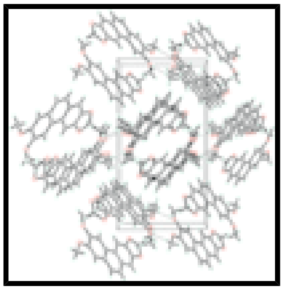


Fig. 2. The packing of the title compound along the *a* axis, H-bonds are shown as dashed lines.

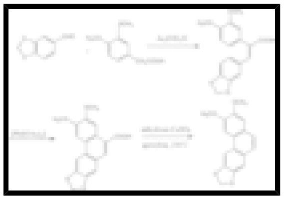


Fig. 3. Reaction Scheme

2,3-Dimethoxy-6,7-methylenedioxyphenanthrene

Crystal data

$C_{17}H_{14}O_4$	F_{000} = 592
M_r = 282.28	D_x = 1.416 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 476 reflections
a = 7.370 (2) Å	θ = 2.4–19.8°
b = 18.375 (5) Å	μ = 0.10 mm^{-1}
c = 9.840 (3) Å	*T* = 293 (2) K
β = 96.363 (4)°	Block, yellow
V = 1324.3 (6) Å^3	0.20 × 0.15 × 0.06 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	2452 independent reflections
Radiation source: fine-focus sealed tube	1011 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.078
T = 293(2) K	θ_{max} = 25.5°
φ and ω scans	θ_{min} = 2.4°
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8 \rightarrow 8$
T_{min} = 0.980, T_{max} = 0.994	$k = -22 \rightarrow 22$
8248 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
2452 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
193 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0039 (7)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.5050 (3)	0.57314 (11)	0.3802 (2)	0.0700 (7)
O2	1.4596 (3)	0.67949 (12)	0.2522 (2)	0.0791 (7)
O3	0.8424 (3)	0.47117 (11)	0.8618 (2)	0.0606 (6)
O4	0.5699 (3)	0.55533 (11)	0.8808 (2)	0.0654 (7)
C1	1.3541 (4)	0.60954 (18)	0.4156 (3)	0.0528 (8)
C2	1.3279 (4)	0.67320 (18)	0.3401 (3)	0.0568 (9)
C3	1.1868 (4)	0.71875 (16)	0.3549 (3)	0.0610 (9)
H3	1.1713	0.7615	0.3045	0.073*
C4	1.0630 (4)	0.69895 (17)	0.4501 (3)	0.0517 (9)
C5	0.9111 (4)	0.74388 (16)	0.4666 (3)	0.0587 (9)
H5	0.8970	0.7872	0.4177	0.070*
C6	0.7854 (4)	0.72569 (16)	0.5513 (3)	0.0561 (9)
H6	0.6867	0.7563	0.5592	0.067*
C7	0.8033 (4)	0.65989 (16)	0.6287 (3)	0.0471 (8)
C8	0.6715 (4)	0.64073 (16)	0.7161 (3)	0.0529 (9)
H8	0.5715	0.6710	0.7217	0.063*
C9	0.6883 (4)	0.57893 (17)	0.7920 (3)	0.0513 (9)
C10	0.8390 (4)	0.53238 (16)	0.7810 (3)	0.0489 (8)
C11	0.9687 (4)	0.54971 (15)	0.6972 (3)	0.0499 (8)
H11	1.0676	0.5187	0.6924	0.060*
C12	0.9550 (4)	0.61436 (16)	0.6173 (3)	0.0448 (8)

C13	1.0876 (4)	0.63338 (16)	0.5259 (3)	0.0455 (8)
C14	1.2392 (4)	0.58828 (15)	0.5059 (3)	0.0523 (8)
H14	1.2589	0.5449	0.5541	0.063*
C15	1.5719 (4)	0.61577 (19)	0.2752 (3)	0.0749 (11)
H15A	1.5682	0.5875	0.1916	0.090*
H15B	1.6975	0.6299	0.3025	0.090*
C16	0.9977 (4)	0.42465 (15)	0.8652 (3)	0.0643 (10)
H16A	1.0101	0.4076	0.7745	0.096*
H16B	0.9822	0.3839	0.9238	0.096*
H16C	1.1053	0.4512	0.8996	0.096*
C17	0.4168 (4)	0.60052 (16)	0.8973 (3)	0.0728 (10)
H17A	0.4587	0.6467	0.9339	0.109*
H17B	0.3421	0.5776	0.9589	0.109*
H17C	0.3466	0.6077	0.8101	0.109*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0601 (15)	0.0798 (17)	0.0734 (17)	0.0039 (13)	0.0226 (13)	0.0136 (13)
O2	0.0748 (18)	0.0823 (18)	0.0852 (18)	−0.0120 (15)	0.0314 (14)	0.0148 (14)
O3	0.0691 (15)	0.0549 (14)	0.0609 (15)	0.0081 (12)	0.0219 (11)	0.0117 (12)
O4	0.0588 (15)	0.0665 (15)	0.0747 (17)	0.0039 (12)	0.0239 (13)	0.0043 (12)
C1	0.048 (2)	0.056 (2)	0.053 (2)	0.0010 (18)	0.0043 (18)	−0.0028 (18)
C2	0.056 (2)	0.058 (2)	0.056 (2)	−0.012 (2)	0.0074 (19)	0.0065 (19)
C3	0.071 (3)	0.045 (2)	0.066 (3)	−0.0108 (19)	0.002 (2)	0.0063 (17)
C4	0.059 (2)	0.045 (2)	0.052 (2)	−0.0040 (18)	0.0047 (18)	0.0012 (17)
C5	0.074 (3)	0.045 (2)	0.056 (2)	0.0018 (19)	0.002 (2)	0.0056 (17)
C6	0.069 (2)	0.045 (2)	0.053 (2)	0.0078 (18)	0.0018 (19)	−0.0018 (17)
C7	0.052 (2)	0.043 (2)	0.045 (2)	−0.0002 (17)	−0.0004 (17)	−0.0057 (16)
C8	0.054 (2)	0.054 (2)	0.051 (2)	0.0064 (17)	0.0051 (18)	−0.0061 (17)
C9	0.047 (2)	0.056 (2)	0.051 (2)	−0.0041 (19)	0.0080 (18)	−0.0055 (18)
C10	0.053 (2)	0.044 (2)	0.048 (2)	−0.0002 (18)	0.0027 (17)	0.0017 (17)
C11	0.051 (2)	0.044 (2)	0.055 (2)	−0.0008 (16)	0.0060 (17)	−0.0027 (17)
C12	0.050 (2)	0.042 (2)	0.042 (2)	0.0026 (16)	0.0017 (16)	−0.0026 (16)
C13	0.052 (2)	0.044 (2)	0.041 (2)	−0.0021 (16)	0.0037 (16)	−0.0045 (16)
C14	0.057 (2)	0.048 (2)	0.053 (2)	0.0011 (17)	0.0072 (18)	0.0035 (16)
C15	0.070 (3)	0.083 (3)	0.075 (3)	−0.010 (2)	0.023 (2)	0.002 (2)
C16	0.072 (2)	0.053 (2)	0.069 (2)	0.0160 (19)	0.0116 (19)	0.0119 (17)
C17	0.057 (2)	0.088 (3)	0.075 (3)	0.008 (2)	0.0192 (19)	−0.009 (2)

Geometric parameters (Å, °)

O1—C1	1.375 (3)	C7—C12	1.410 (3)
O1—C15	1.428 (3)	C7—C8	1.411 (4)
O2—C2	1.375 (3)	C8—C9	1.357 (3)
O2—C15	1.437 (3)	C8—H8	0.9300
O3—C10	1.376 (3)	C9—C10	1.416 (4)
O3—C16	1.426 (3)	C10—C11	1.367 (3)
O4—C9	1.372 (3)	C11—C12	1.422 (3)

O4—C17	1.424 (3)	C11—H11	0.9300
C1—C14	1.351 (4)	C12—C13	1.443 (4)
C1—C2	1.387 (4)	C13—C14	1.422 (3)
C2—C3	1.355 (4)	C14—H14	0.9300
C3—C4	1.426 (4)	C15—H15A	0.9700
C3—H3	0.9300	C15—H15B	0.9700
C4—C5	1.415 (4)	C16—H16A	0.9600
C4—C13	1.418 (4)	C16—H16B	0.9600
C5—C6	1.355 (4)	C16—H16C	0.9600
C5—H5	0.9300	C17—H17A	0.9600
C6—C7	1.427 (3)	C17—H17B	0.9600
C6—H6	0.9300	C17—H17C	0.9600

C1—O1—C15	105.7 (2)	C11—C10—C9	120.8 (3)
C2—O2—C15	105.5 (2)	O3—C10—C9	114.5 (3)
C10—O3—C16	117.8 (2)	C10—C11—C12	121.1 (3)
C9—O4—C17	117.1 (2)	C10—C11—H11	119.5
C14—C1—O1	127.5 (3)	C12—C11—H11	119.5
C14—C1—C2	122.4 (3)	C7—C12—C11	117.4 (3)
O1—C1—C2	110.1 (3)	C7—C12—C13	120.2 (3)
C3—C2—O2	128.2 (3)	C11—C12—C13	122.4 (3)
C3—C2—C1	121.8 (3)	C4—C13—C14	118.6 (3)
O2—C2—C1	110.0 (3)	C4—C13—C12	118.6 (3)
C2—C3—C4	117.9 (3)	C14—C13—C12	122.8 (3)
C2—C3—H3	121.1	C1—C14—C13	118.8 (3)
C4—C3—H3	121.1	C1—C14—H14	120.6
C5—C4—C13	119.5 (3)	C13—C14—H14	120.6
C5—C4—C3	119.9 (3)	O1—C15—O2	108.8 (2)
C13—C4—C3	120.6 (3)	O1—C15—H15A	109.9
C6—C5—C4	122.0 (3)	O2—C15—H15A	109.9
C6—C5—H5	119.0	O1—C15—H15B	109.9
C4—C5—H5	119.0	O2—C15—H15B	109.9
C5—C6—C7	120.5 (3)	H15A—C15—H15B	108.3
C5—C6—H6	119.7	O3—C16—H16A	109.5
C7—C6—H6	119.7	O3—C16—H16B	109.5
C12—C7—C8	120.3 (3)	H16A—C16—H16B	109.5
C12—C7—C6	119.2 (3)	O3—C16—H16C	109.5
C8—C7—C6	120.5 (3)	H16A—C16—H16C	109.5
C9—C8—C7	121.1 (3)	H16B—C16—H16C	109.5
C9—C8—H8	119.4	O4—C17—H17A	109.5
C7—C8—H8	119.4	O4—C17—H17B	109.5
C8—C9—O4	126.1 (3)	H17A—C17—H17B	109.5
C8—C9—C10	119.2 (3)	O4—C17—H17C	109.5
O4—C9—C10	114.7 (3)	H17A—C17—H17C	109.5
C11—C10—O3	124.7 (3)	H17B—C17—H17C	109.5

C15—O1—C1—C14	176.3 (3)	O4—C9—C10—C11	−179.3 (2)
C15—O1—C1—C2	−1.5 (3)	C8—C9—C10—O3	−179.7 (2)
C15—O2—C2—C3	−178.2 (3)	O4—C9—C10—O3	−0.3 (4)
C15—O2—C2—C1	0.3 (3)	O3—C10—C11—C12	−179.8 (2)

C14—C1—C2—C3	1.4 (5)	C9—C10—C11—C12	−0.9 (4)
O1—C1—C2—C3	179.4 (3)	C8—C7—C12—C11	−0.3 (4)
C14—C1—C2—O2	−177.2 (3)	C6—C7—C12—C11	179.3 (2)
O1—C1—C2—O2	0.8 (4)	C8—C7—C12—C13	178.8 (3)
O2—C2—C3—C4	177.6 (3)	C6—C7—C12—C13	−1.6 (4)
C1—C2—C3—C4	−0.7 (5)	C10—C11—C12—C7	0.4 (4)
C2—C3—C4—C5	−178.5 (3)	C10—C11—C12—C13	−178.7 (3)
C2—C3—C4—C13	−0.3 (4)	C5—C4—C13—C14	178.8 (3)
C13—C4—C5—C6	−1.1 (4)	C3—C4—C13—C14	0.6 (4)
C3—C4—C5—C6	177.1 (3)	C5—C4—C13—C12	0.4 (4)
C4—C5—C6—C7	0.5 (5)	C3—C4—C13—C12	−177.8 (3)
C5—C6—C7—C12	0.9 (4)	C7—C12—C13—C4	0.9 (4)
C5—C6—C7—C8	−179.5 (3)	C11—C12—C13—C4	180.0 (3)
C12—C7—C8—C9	0.8 (4)	C7—C12—C13—C14	−177.4 (3)
C6—C7—C8—C9	−178.9 (3)	C11—C12—C13—C14	1.6 (4)
C7—C8—C9—O4	179.4 (3)	O1—C1—C14—C13	−178.6 (3)
C7—C8—C9—C10	−1.2 (4)	C2—C1—C14—C13	−1.0 (4)
C17—O4—C9—C8	−1.4 (4)	C4—C13—C14—C1	0.0 (4)
C17—O4—C9—C10	179.2 (2)	C12—C13—C14—C1	178.4 (3)
C16—O3—C10—C11	4.1 (4)	C1—O1—C15—O2	1.7 (3)
C16—O3—C10—C9	−174.9 (2)	C2—O2—C15—O1	−1.2 (3)
C8—C9—C10—C11	1.3 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17B···O3^{i}	0.96	2.51	3.465 (3)	174

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

Fig. 1

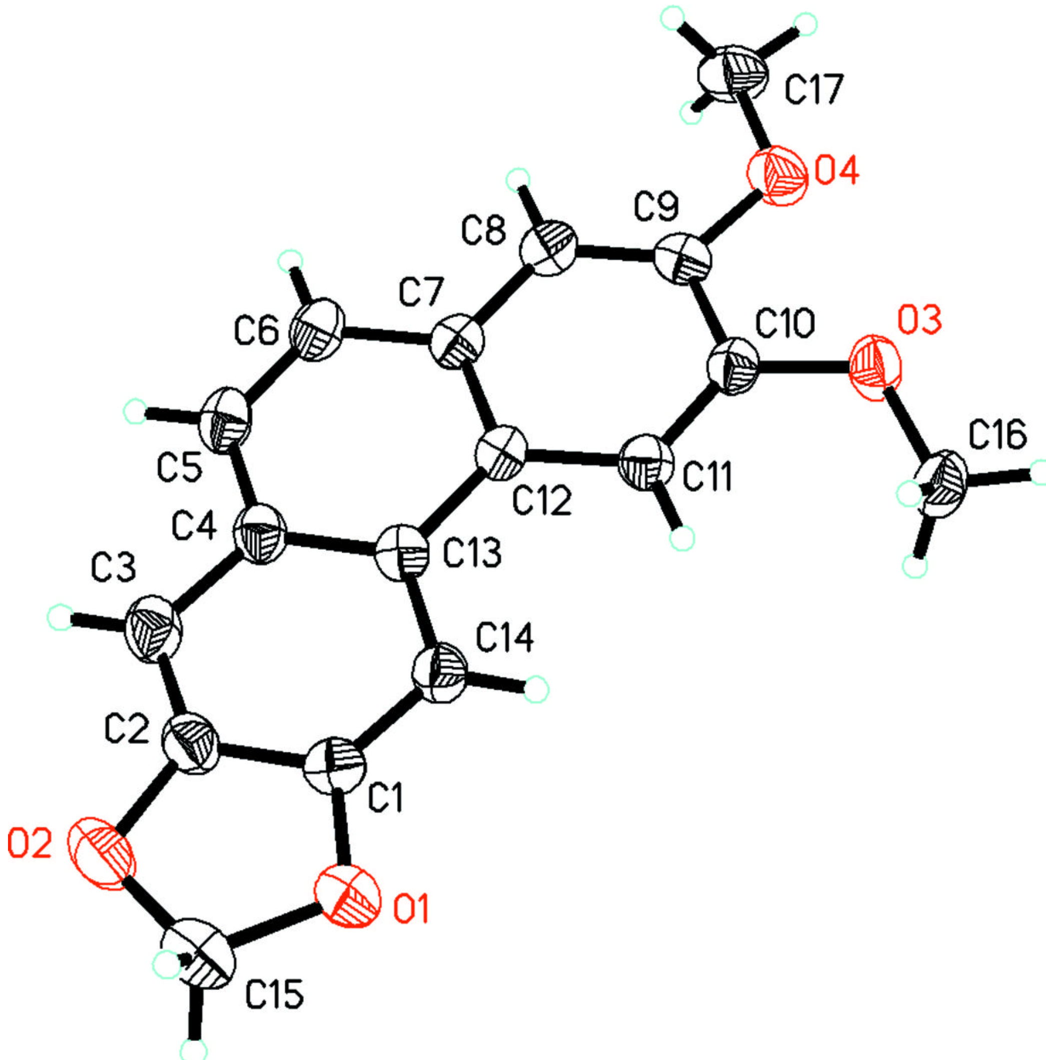

C17
O4
C9
C8
C7
C10
O3
C6
C16
C5
C12
C11
C4
C13
C3
C14
C2
C1
O2
O1
C15

Fig. 2

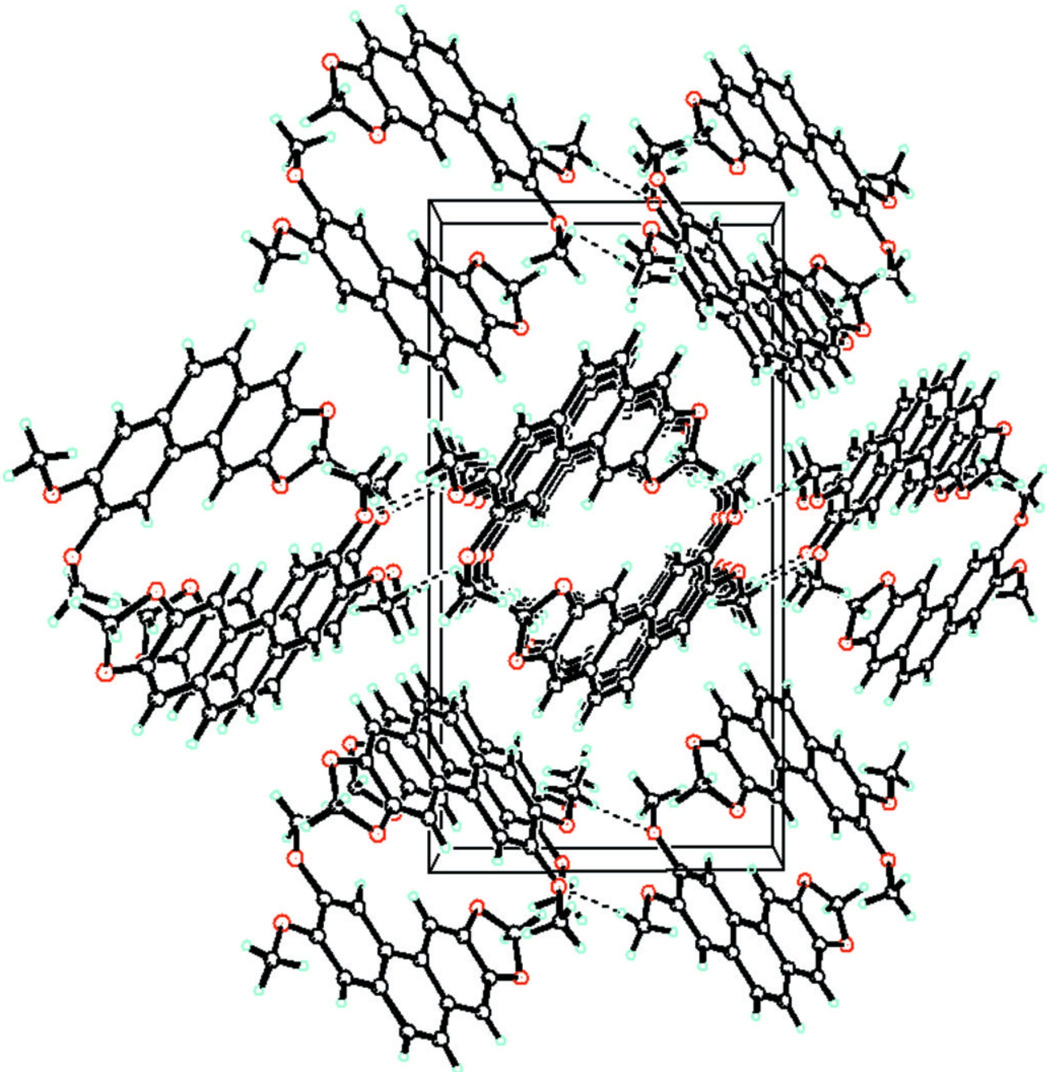
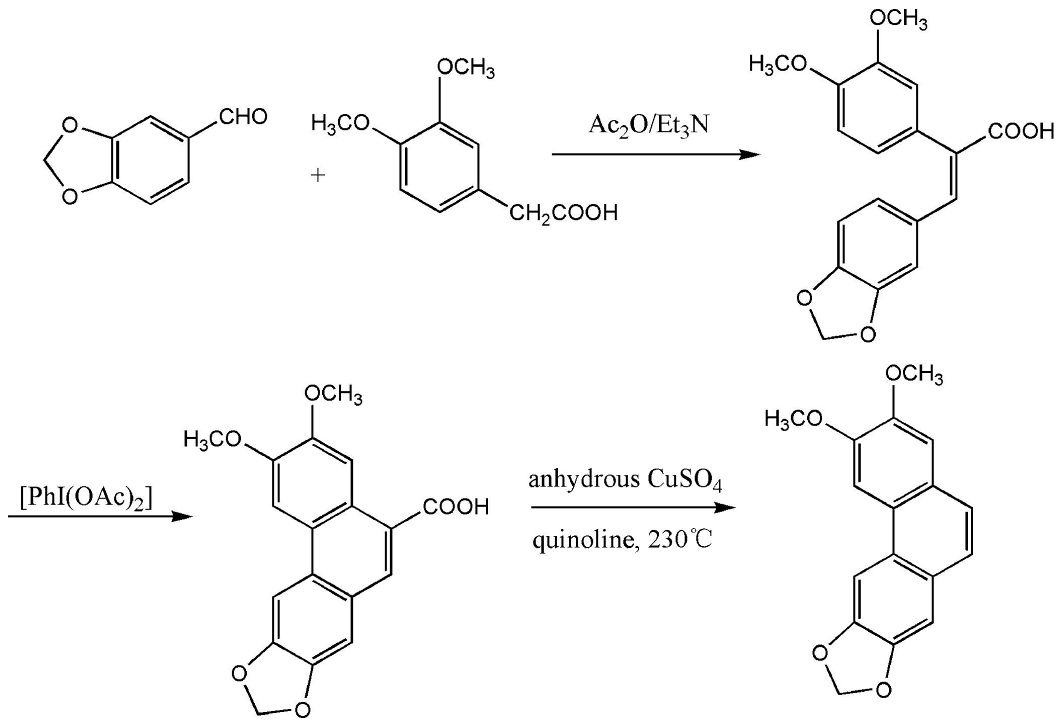


Fig. 3


CHO
OCH3
H3CO
CH2COOH
Ac2O/Et3N
COOH
[PhI(OAc)2]
anhydrous CuSO4
quinoline, 230℃