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8-Methoxy-3,4-methylenedioxy-10-nitrophenanthrene-1-carboxylic acid

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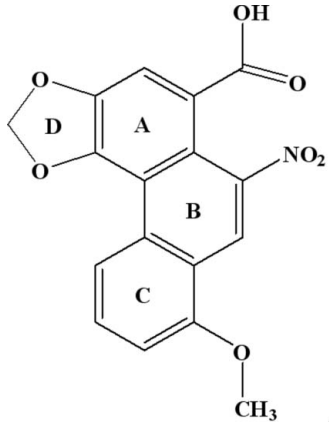
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.051; wR factor = 0.137; data-to-parameter ratio = 11.7.

In the crystal structure of the title compound, $C_{17}H_{11}NO_7$, the phenanthrene ring system and the five-membered ring are almost coplanar. The carboxy and nitro groups lie above and below the plane, respectively, owing to steric effects. The hydroxy groups form strong intermolecular O—H···O hydrogen bonds with the carbonyl group O atom. The carboxy groups of pairs of molecules form centrosymmetric rings *via* pairs of intermolecular hydrogen bonds.

Related literature

For related literature, see: Gu *et al.* (2005).



Experimental

Crystal data

$C_{17}H_{11}NO_7$
M_r = 341.27
Monoclinic, $C2/c$
a = 19.695 (2) Å
b = 9.050 (1) Å
c = 18.986 (1) Å
β = 119.483 (5)°
V = 2945.8 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 295 (2) K
0.50 × 0.40 × 0.30 mm

Data collection

MAC DIP 2030K diffractometer
Absorption correction: none
4831 measured reflections
2667 independent reflections
2208 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.137
S = 1.02
2667 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O4^{i}	0.82	1.82	2.6330 (16)	174

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

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2338).

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Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
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supplementary materials

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8-Methoxy-3,4-methylenedioxy-10-nitrophenanthrene-1-carboxylic acid

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Comment

The title compound,(I), which is also known as Aristolochic Acid, was extracted from A. manshuriensis Kom with methanol (Gu *et al.*, 2005). The compound was crystallized from acetone and its structure is reported here.

The phenanthrene ring is substantially planar. The dihedral angle between ring A and ring B 3.9 (1)° as a result of steric effects from the carboxy group and nitro group which lie above and below the plane respectively. The torsion angle C16—C1—C11—C10 is −13.0 (3)°. The torsion angle N1—C10—C11—C1 is −19.2 (3)°. Ring D is planar, with the dihedral angle between the ring A and ring D 0.8 (2)°. The torsion angle C6—C7—C8—O7 is −178.5 (3)°. The methyl and the nitro group are on the same side of the plane.

The hydroxy group and the O atom of the carbonyl group form strong intermolecular O—H···O hydrogen bonds (Table 1). The carboxy group at (*x*, *y*, *z*) and the carboxy group at (1/2 − *x*, 1/2 − *y*, −*z*) form a ring *via* pairs of intermolecular hydrogen bonds. In the crystal structure, these rings form a serial of interlacing weak interactions which are vital for the stability of the crystal structure. The hydrogen-bonding arrangement is shown in Fig. 2.

Experimental

The title compound was prepared according to the procedure of Gu *et al.* (2005) from the herb A. manshuriensis Kom. Crystals appropriate for data collection were obtained from acetone solution, yielding yellow plate-like crystals after four days at room temperature.

Refinement

The carboxylic acid H atom was initially located in a difference Fourier map and constrained to ride on its parent atom with the O—H distance 0.82 Å and with U_{iso}(H) = 1.5U_{eq}(O). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.92–0.99 Å and with U_{iso}(H) = 1.2(1.5 for methyl groups)U_{eq}(C).

Figures

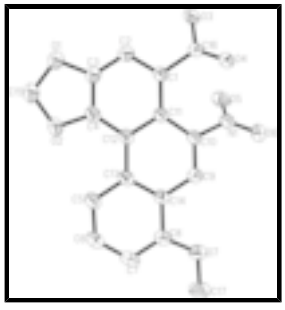

Fig. 1. View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

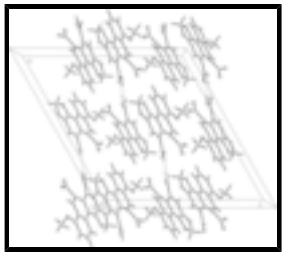

Fig. 2. The molecular packing of (I) viewed along the *b* axis. Dash lines indicate the hydrogen bonding interactions.

8-Methoxy-3,4-methylenedioxy-10-nitrophenanthrene-1-carboxylic acid

Crystal data

$C_{17}H_{11}N_1O_7$	F_{000} = 1408
M_r = 341.27	D_x = 1.539 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2667 reflections
a = 19.695 (2) Å	θ = 2.4–25.4º
b = 9.050 (1) Å	μ = 0.12 mm^{-1}
c = 18.986 (1) Å	*T* = 295 (2) K
β = 119.483 (5)º	Plate, yellow
V = 2945.8 (5) Å^3	0.50 × 0.40 × 0.30 mm
Z = 8	

Data collection

MAC DIP 2030K diffractometer	2208 reflections with $I > 2\sigma(I)$
Radiation source: rotate anode	R_{int} = 0.032
Monochromator: graphite	θ_{max} = 25.4º
T = 295(2) K	θ_{min} = 2.4º
ω scans	*h* = 0→23
Absorption correction: none	*k* = 0→10
4831 measured reflections	*l* = −22→19
2667 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.051	$w = 1/[\sigma^2(F_o^2) + (0.0841P)^2 + 0.8932P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.137	$(\Delta/\sigma)_{max} < 0.001$
S = 1.02	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
2667 reflections	$\Delta\rho_{min}$ = −0.25 e Å^{-3}

227 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.073 (4)

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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.39126 (8)	−0.03249 (18)	0.65245 (9)	0.0619 (4)
O1	0.59263 (8)	0.36643 (16)	0.53372 (11)	0.0858 (5)
O2	0.65875 (7)	0.14805 (16)	0.58614 (10)	0.0767 (4)
O3	0.33911 (7)	0.35127 (14)	0.53900 (9)	0.0709 (4)
H3A	0.2919	0.3570	0.5211	0.106*
O4	0.31135 (7)	0.11097 (13)	0.51660 (8)	0.0623 (4)
O5	0.39179 (8)	0.08442 (17)	0.68474 (9)	0.0758 (4)
O6	0.34436 (8)	−0.13248 (17)	0.63900 (10)	0.0835 (5)
O7	0.55873 (9)	−0.45721 (16)	0.71258 (10)	0.0845 (5)
C1	0.44277 (9)	0.19015 (19)	0.56666 (10)	0.0554 (4)
C2	0.47687 (10)	0.3006 (2)	0.54393 (11)	0.0634 (5)
H2A	0.4513	0.3894	0.5223	0.076*
C3	0.54982 (11)	0.2736 (2)	0.55471 (12)	0.0638 (5)
C4	0.58857 (9)	0.1440 (2)	0.58507 (10)	0.0584 (4)
C5	0.67215 (10)	−0.1437 (2)	0.64861 (11)	0.0645 (5)
H5A	0.6980	−0.0725	0.6352	0.077*
C6	0.70591 (11)	−0.2797 (2)	0.67650 (12)	0.0731 (5)
H6A	0.7541	−0.2993	0.6807	0.088*
C7	0.67046 (12)	−0.3884 (2)	0.69862 (12)	0.0728 (5)
H7A	0.6950	−0.4789	0.7182	0.087*
C8	0.59874 (11)	−0.3612 (2)	0.69135 (11)	0.0646 (5)
C9	0.48868 (9)	−0.19269 (19)	0.65732 (10)	0.0573 (4)
H9A	0.4647	−0.2656	0.6720	0.069*
C10	0.45406 (9)	−0.05946 (19)	0.63288 (10)	0.0543 (4)
C11	0.48282 (9)	0.05599 (18)	0.60243 (9)	0.0509 (4)
C12	0.55825 (9)	0.02811 (18)	0.61000 (9)	0.0538 (4)
C13	0.59829 (9)	−0.11214 (19)	0.64024 (9)	0.0548 (4)
C14	0.56104 (10)	−0.22350 (19)	0.66104 (10)	0.0561 (4)

C15	0.66290 (12)	0.2899 (3)	0.55530 (16)	0.0825 (6)
H15A	0.7070	0.3450	0.5962	0.099*
H15B	0.6697	0.2786	0.5083	0.099*
C16	0.35875 (10)	0.21296 (19)	0.54018 (10)	0.0553 (4)
C17	0.59882 (17)	−0.5836 (3)	0.75850 (18)	0.1008 (8)
H17A	0.5642	−0.6415	0.7694	0.151*
H17B	0.6428	−0.5529	0.8086	0.151*
H17C	0.6166	−0.6419	0.7285	0.151*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0520 (8)	0.0651 (9)	0.0695 (8)	0.0103 (7)	0.0305 (7)	0.0147 (7)
O1	0.0677 (9)	0.0649 (8)	0.1334 (13)	−0.0056 (7)	0.0561 (9)	0.0141 (8)
O2	0.0552 (7)	0.0706 (9)	0.1121 (11)	−0.0035 (6)	0.0472 (7)	0.0015 (7)
O3	0.0528 (7)	0.0561 (8)	0.0964 (9)	0.0081 (6)	0.0310 (7)	0.0004 (6)
O4	0.0484 (6)	0.0573 (7)	0.0757 (7)	0.0040 (5)	0.0264 (6)	0.0056 (6)
O5	0.0770 (9)	0.0787 (9)	0.0815 (8)	0.0180 (7)	0.0466 (7)	0.0017 (7)
O6	0.0615 (8)	0.0797 (10)	0.1170 (11)	0.0019 (7)	0.0498 (8)	0.0186 (8)
O7	0.0802 (9)	0.0654 (9)	0.1126 (11)	0.0216 (7)	0.0509 (8)	0.0295 (8)
C1	0.0484 (9)	0.0524 (9)	0.0610 (9)	0.0017 (7)	0.0234 (7)	0.0001 (7)
C2	0.0539 (9)	0.0535 (10)	0.0779 (11)	0.0035 (8)	0.0287 (8)	0.0052 (8)
C3	0.0567 (10)	0.0564 (10)	0.0770 (11)	−0.0072 (8)	0.0320 (8)	−0.0005 (8)
C4	0.0461 (8)	0.0598 (10)	0.0677 (9)	−0.0052 (7)	0.0267 (7)	−0.0072 (8)
C5	0.0487 (9)	0.0690 (11)	0.0725 (10)	0.0056 (8)	0.0273 (8)	−0.0022 (8)
C6	0.0538 (10)	0.0795 (13)	0.0836 (12)	0.0150 (9)	0.0320 (9)	−0.0013 (10)
C7	0.0653 (11)	0.0672 (12)	0.0795 (12)	0.0226 (9)	0.0307 (9)	0.0060 (9)
C8	0.0644 (10)	0.0594 (11)	0.0677 (10)	0.0117 (8)	0.0308 (8)	0.0059 (8)
C9	0.0514 (9)	0.0552 (9)	0.0627 (9)	0.0034 (7)	0.0261 (7)	0.0044 (7)
C10	0.0439 (8)	0.0574 (9)	0.0590 (8)	0.0039 (7)	0.0234 (7)	0.0019 (7)
C11	0.0435 (8)	0.0512 (8)	0.0532 (8)	0.0020 (6)	0.0202 (6)	−0.0014 (6)
C12	0.0441 (8)	0.0546 (9)	0.0579 (8)	−0.0007 (7)	0.0213 (7)	−0.0045 (7)
C13	0.0472 (8)	0.0575 (9)	0.0546 (8)	0.0037 (7)	0.0211 (7)	−0.0034 (7)
C14	0.0507 (9)	0.0545 (9)	0.0584 (8)	0.0076 (7)	0.0232 (7)	0.0002 (7)
C15	0.0639 (12)	0.0758 (14)	0.1143 (16)	−0.0106 (10)	0.0489 (12)	0.0032 (12)
C16	0.0492 (8)	0.0521 (9)	0.0606 (9)	0.0056 (7)	0.0239 (7)	0.0050 (7)
C17	0.1043 (18)	0.0868 (16)	0.1176 (18)	0.0369 (14)	0.0593 (16)	0.0464 (14)

Geometric parameters (Å, °)

N1—O5	1.220 (2)	C5—C13	1.413 (2)
N1—O6	1.227 (2)	C5—H5A	0.9300
N1—C10	1.476 (2)	C6—C7	1.386 (3)
O1—C3	1.381 (2)	C6—H6A	0.9300
O1—C15	1.416 (3)	C7—C8	1.372 (3)
O2—C4	1.373 (2)	C7—H7A	0.9300
O2—C15	1.430 (3)	C8—C14	1.419 (2)
O3—C16	1.307 (2)	C9—C10	1.350 (2)
O3—H3A	0.8200	C9—C14	1.419 (2)

O4—C16	1.230 (2)	C9—H9A	0.9300
O7—C8	1.361 (2)	C10—C11	1.439 (2)
O7—C17	1.419 (3)	C11—C12	1.443 (2)
C1—C2	1.386 (3)	C12—C13	1.455 (2)
C1—C11	1.425 (2)	C13—C14	1.412 (2)
C1—C16	1.488 (2)	C15—H15A	0.9700
C2—C3	1.370 (3)	C15—H15B	0.9700
C2—H2A	0.9300	C17—H17A	0.9600
C3—C4	1.363 (3)	C17—H17B	0.9600
C4—C12	1.399 (2)	C17—H17C	0.9600
C5—C6	1.375 (3)		
O5—N1—O6	124.3 (2)	C10—C9—H9A	119.4
O5—N1—C10	117.9 (2)	C14—C9—H9A	119.4
O6—N1—C10	117.6 (2)	C9—C10—C11	123.7 (2)
C3—O1—C15	105.5 (2)	C9—C10—N1	113.9 (2)
C4—O2—C15	106.2 (2)	C11—C10—N1	121.7 (2)
C16—O3—H3A	109.5	C1—C11—C10	125.1 (2)
C8—O7—C17	117.9 (2)	C1—C11—C12	119.8 (2)
C2—C1—C11	121.5 (2)	C10—C11—C12	115.1 (2)
C2—C1—C16	115.1 (2)	C4—C12—C11	115.1 (2)
C11—C1—C16	122.8 (2)	C4—C12—C13	123.3 (2)
C3—C2—C1	117.3 (2)	C11—C12—C13	121.5 (2)
C3—C2—H2A	121.4	C14—C13—C5	118.2 (2)
C1—C2—H2A	121.4	C14—C13—C12	118.5 (2)
C4—C3—C2	122.9 (2)	C5—C13—C12	123.3 (2)
C4—C3—O1	110.6 (2)	C13—C14—C9	119.5 (2)
C2—C3—O1	126.4 (2)	C13—C14—C8	119.9 (2)
C3—C4—O2	109.5 (2)	C9—C14—C8	120.3 (2)
C3—C4—C12	123.0 (2)	O1—C15—O2	108.2 (2)
O2—C4—C12	127.5 (2)	O1—C15—H15A	110.0
C6—C5—C13	120.1 (2)	O2—C15—H15A	110.0
C6—C5—H5A	120.0	O1—C15—H15B	110.0
C13—C5—H5A	120.0	O2—C15—H15B	110.0
C5—C6—C7	122.1 (2)	H15A—C15—H15B	108.4
C5—C6—H6A	118.9	O4—C16—O3	123.2 (2)
C7—C6—H6A	118.9	O4—C16—C1	122.5 (2)
C8—C7—C6	119.2 (2)	O3—C16—C1	114.2 (2)
C8—C7—H7A	120.4	O7—C17—H17A	109.5
C6—C7—H7A	120.4	O7—C17—H17B	109.5
O7—C8—C7	124.9 (2)	H17A—C17—H17B	109.5
O7—C8—C14	114.6 (2)	O7—C17—H17C	109.5
C7—C8—C14	120.4 (2)	H17A—C17—H17C	109.5
C10—C9—C14	121.2 (2)	H17B—C17—H17C	109.5
C11—C1—C2—C3	2.2 (3)	N1—C10—C11—C12	161.4 (2)
C16—C1—C2—C3	−169.3 (2)	C3—C4—C12—C11	−0.8 (2)
C1—C2—C3—C4	1.1 (3)	O2—C4—C12—C11	179.5 (2)
C1—C2—C3—O1	177.7 (2)	C3—C4—C12—C13	178.1 (2)
C15—O1—C3—C4	−2.0 (2)	O2—C4—C12—C13	−1.5 (3)

C15—O1—C3—C2	−179.0 (2)	C1—C11—C12—C4	3.9 (2)
C2—C3—C4—O2	177.9 (2)	C10—C11—C12—C4	−176.2 (2)
O1—C3—C4—O2	0.8 (2)	C1—C11—C12—C13	−175.1 (2)
C2—C3—C4—C12	−1.7 (3)	C10—C11—C12—C13	4.8 (2)
O1—C3—C4—C12	−178.8 (2)	C6—C5—C13—C14	−0.1 (3)
C15—O2—C4—C3	0.7 (2)	C6—C5—C13—C12	−179.1 (2)
C15—O2—C4—C12	−179.6 (2)	C4—C12—C13—C14	−177.7 (2)
C13—C5—C6—C7	−1.2 (3)	C11—C12—C13—C14	1.2 (2)
C5—C6—C7—C8	1.1 (3)	C4—C12—C13—C5	1.1 (3)
C17—O7—C8—C7	11.7 (3)	C11—C12—C13—C5	−179.9 (2)
C17—O7—C8—C14	−167.2 (2)	C5—C13—C14—C9	176.7 (2)
C6—C7—C8—O7	−178.5 (2)	C12—C13—C14—C9	−4.3 (2)
C6—C7—C8—C14	0.4 (3)	C5—C13—C14—C8	1.6 (2)
C14—C9—C10—C11	5.5 (3)	C12—C13—C14—C8	−179.5 (2)
C14—C9—C10—N1	−164.9 (2)	C10—C9—C14—C13	1.2 (2)
O5—N1—C10—C9	131.4 (2)	C10—C9—C14—C8	176.3 (2)
O6—N1—C10—C9	−44.9 (2)	O7—C8—C14—C13	177.3 (2)
O5—N1—C10—C11	−39.3 (2)	C7—C8—C14—C13	−1.7 (3)
O6—N1—C10—C11	144.5 (2)	O7—C8—C14—C9	2.1 (2)
C2—C1—C11—C10	175.4 (2)	C7—C8—C14—C9	−176.8 (2)
C16—C1—C11—C10	−13.8 (2)	C3—O1—C15—O2	2.4 (2)
C2—C1—C11—C12	−4.8 (2)	C4—O2—C15—O1	−1.9 (2)
C16—C1—C11—C12	166.1 (2)	C2—C1—C16—O4	141.4 (2)
C9—C10—C11—C1	171.5 (2)	C11—C1—C16—O4	−29.9 (2)
N1—C10—C11—C1	−18.7 (2)	C2—C1—C16—O3	−34.1 (2)
C9—C10—C11—C12	−8.3 (2)	C11—C1—C16—O3	154.5 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O4^{i}	0.82	1.82	2.6330 (16)	174

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

Fig. 1

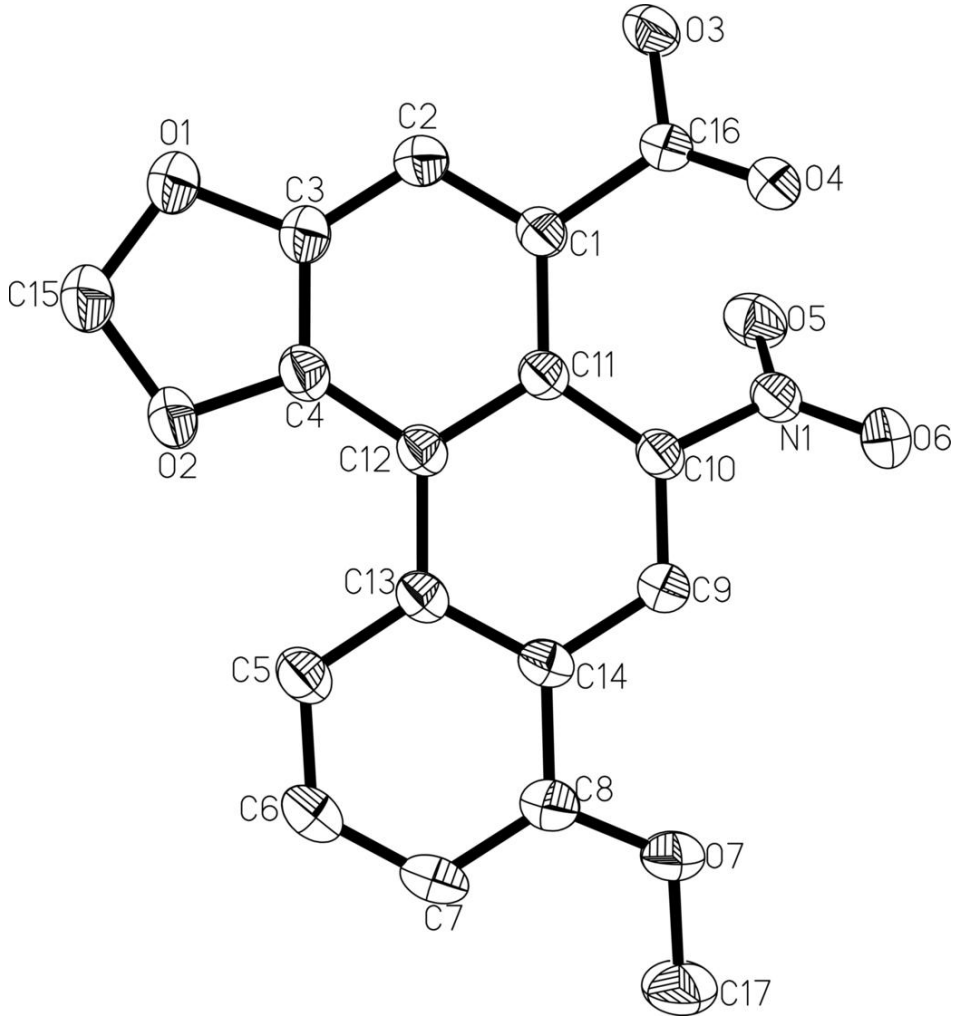
O3
C2
O1
C16
O4
C3
C1
C15
O5
C11
C4
N1
O6
O2
C12
C10
C13
C9
C5
C14
C8
C6
O7
C7
C17

Fig. 2