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A [4π+4π] intramolecular photocyclomer of 9-anthroic anhydride: 5,6,11,12-tetrahydro-5,12;6,11-di-*o*-benzenodibenzo[*a*,*e*]cyclooctene-5,6-dicarboxylic anhydride

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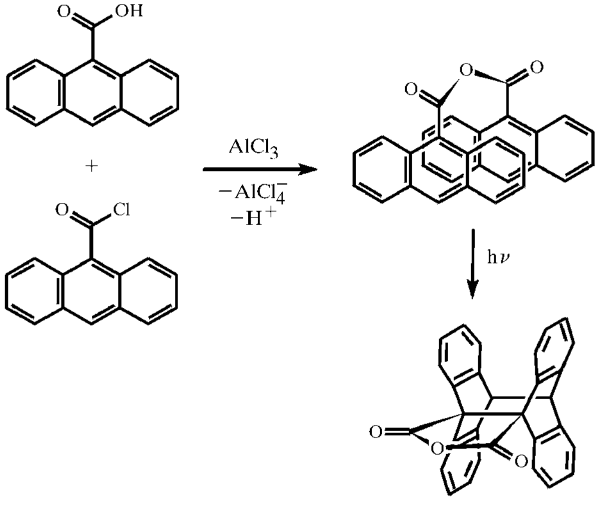
The title compound, $C_{30}H_{18}O_3$, was obtained by light irradiation of a dichloroethane solution of 9-anthroyl chloride and 9-anthroic acid. The molecules, which possess approximately *mm*2 local symmetry, are packed in columns, the oxygenated moieties facing each other according to the symmetry of a monoclinic lattice. The space group of the crystal is $P2_1/c$, with a whole molecule as the asymmetric unit. The structure is compared with those of similar dianthracene derivatives.

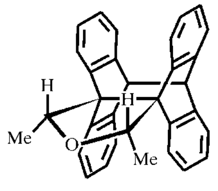
Comment

The title compound, (I), was first obtained by sunlight irradiation of a solution of 9-anthroic anhydride (Greene *et al.*, 1955). In the course of the preparation of some anthroyl-functionalized β-ketoenolate derivatives of rhodium(III) and iridium(III) (Carano *et al.*, 2002), we have found that (I) is formed as a by-product of the reaction between Rh(acac)$_3$ or Ir(acac)$_3$ (acac is pentane-2,4-dionate) and 9-anthroyl chloride in the presence of AlCl$_3$. The genesis of (I) is easily rationalized according to the reactions outlined in the *Scheme* below, which imply the presence of 9-anthroic acid as an impurity. Indeed, the ^{1}H NMR spectrum of the mixture resulting from the reaction of 9-anthroyl chloride with 9-anthroic acid, at 253 K in the presence of AlCl$_3$, indicated the presence of 9-anthroic anhydride. Exposure of this solution to sunlight resulted in the slow deposition of well shaped crystals of (I). Since compounds resulting from the [4π + 4π] cycloaddition of two anthracene moieties are currently of great interest (Becker, 1993; Bouas-Laurent *et al.*, 2000), we characterized (I) by single-crystal X-ray analysis.

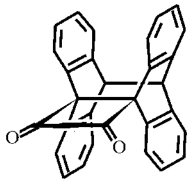
The molecular structure of (I) is shown in Fig. 1, and bond distances and angles are listed in Table 1. The geometric parameters of the aromatic moiety are very similar to those already reported for 9,9′:10,10′-dianthracene (Ehrenberg, 1966; Choi & Marinkas, 1980; Abboud *et al.*, 1990). Indeed, very long C1—C15 and C8—C22 bonds [1.614 (5) and 1.612 (5) Å, respectively] are observed, along with a bending of the anthrylidene moieties, as a result of the *sp*^{3} hybridization of atoms C1, C8, C15 and C22. The two anthrylidene moieties of (I) show a difference in bending of 130.8 (1) and 134.9 (1)°, respectively. Slightly different dihedral angles are also observed between the C1–C8 and C15–C22 planes [47.6 (1)°], and between the C8–C14/C1 and C22–C28/C15 planes [46.7 (1)°]. These differences, which probably arise from the packing forces, reduce the *mm*2 molecular symmetry. Similar distortions are found in other dianthracene derivatives in which the C1—C15 bond is shared with a condensed five- [(II); Noe *et al.*, 1994] or four-membered ring [(III); Becker *et al.*, 1991] (see *Scheme* below).



(I)



(II)



(III)

Within this class of compounds, maximum crystallographic symmetry has been observed only in the molecular structure of 9,9′:10,10′-dianthracene, which is centrosymmetric. Atoms C1 and C15 of (I) are part of an almost perfectly planar (maximum deviation 0.01 Å) oxacyclopentanedione ring (anhydride) whose geometrical parameters, apart from the unusual length of the C1—C15 bond, are very similar to those of succinic anhydride (Ehrenberg, 1965; Biagini & Cannas, 1965; Fodor *et al.*, 1984).

The crystal structure of (I), shown in Fig. 2, is built up of double columns of molecules extending in the *a* direction. The molecules along the double columns are related by inversion centres (Wyckoff position 2*c*), which force the oxygenated moieties to face each other. As atom O2, which occupies the central position in the molecule, is positioned at $x = 0.7516$ (3),

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the molecules along the double columns are spanned by almost exactly $\frac{a}{2}$. In the other two directions, as shown in Fig. 2, the double columns are disposed as a herring-bone. Almost all the intermolecular contacts are greater than or equal to the sum of the van der Waals radii of the atoms involved (Bondi, 1964; Nyburg & Faerman, 1985; Nyburg *et al.*, 1987), with the sole exception of the distance between atoms O3 and H24, *i.e.* the H atom linked to atom C24 (Table 2). This short contact, although corresponding to a weak interaction, is probably of some relevance in the packing.

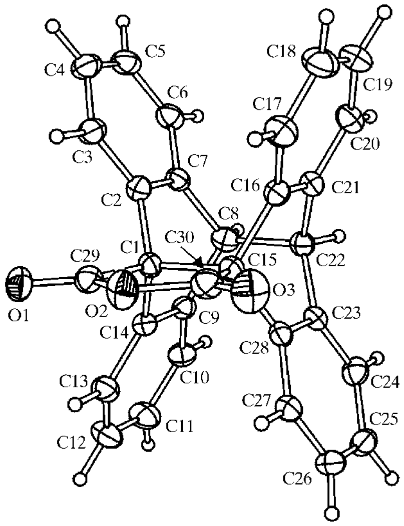

Figure 1
A view of the structure of (I) showing 30% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

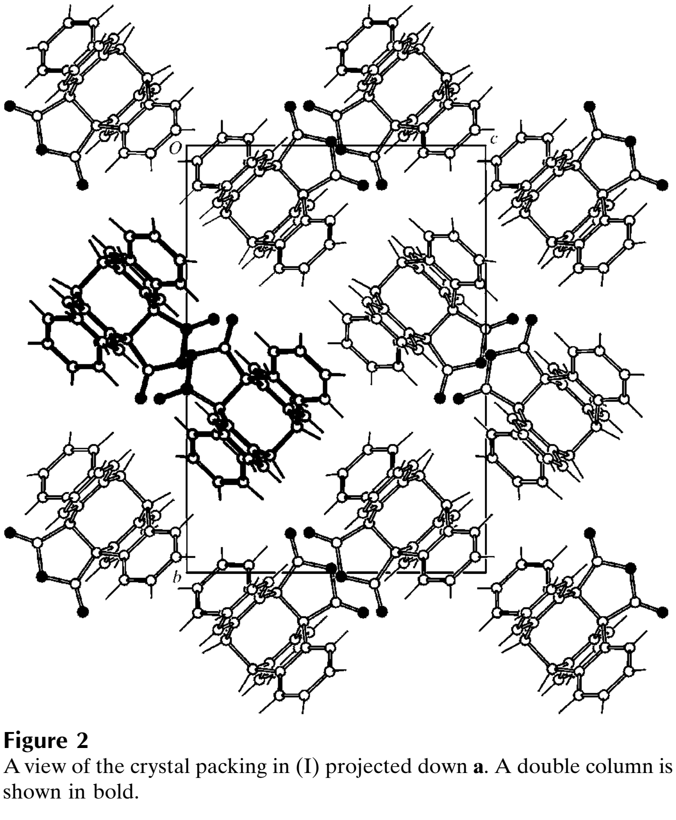

Figure 2
A view of the crystal packing in (I) projected down **a**. A double column is shown in bold.

Experimental

Compound (I) is a by-product of the reaction of *M*(acac)$_3$ (*M* is Rh or Ir) with 9-anthroyl chloride and AlCl$_3$ at 253 K, in dichloroethane. The reaction mixture was treated with 10% aqueous HCl at 273 K. The organic layer was then separated and dried over anhydrous Na$_2$SO$_4$. After evaporation of the volatiles under vacuum, a solid residue was obtained which was dissolved in CH$_2$Cl$_2$. Well shaped crystals of (I) were obtained from the resulting solution by slow evaporation of the solvent at room temperature.

Crystal data

$C_{30}H_{18}O_3$
M_r = 426.44
Monoclinic, $P2_1/c$
a = 10.1635 (17) Å
b = 17.038 (3) Å
c = 12.547 (3) Å
β = 108.155 (13)°
V = 2064.5 (7) Å^3
Z = 4

D_x = 1.372 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
θ = 6.3–17.1°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism flattened on (100), colourless
0.35 × 0.32 × 0.11 mm

Data collection

Bruker P4 diffractometer
$2\theta/\omega$ scans
4826 measured reflections
3822 independent reflections
1769 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.050
$\theta_{\rm max}$ = 25.5°

$h = -10 \rightarrow 12$
$k = -1 \rightarrow 20$
$l = -15 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.066
$wR(F^2)$ = 0.138
S = 0.98
3822 reflections
370 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C29	1.510 (5)	C15—C28	1.522 (5)
C1—C14	1.535 (5)	C15—C16	1.531 (5)
C1—C2	1.539 (5)	C21—C22	1.512 (5)
C1—C15	1.614 (5)	C22—C23	1.516 (5)
C7—C8	1.510 (5)	C29—O1	1.187 (4)
C8—C9	1.508 (5)	C29—O2	1.391 (4)
C8—C22	1.612 (5)	O2—C30	1.381 (5)
C15—C30	1.515 (5)	C30—O3	1.192 (4)
C29—C1—C14	110.4 (3)	C28—C15—C1	111.3 (3)
C29—C1—C2	110.7 (3)	C16—C15—C1	112.3 (3)
C14—C1—C2	108.4 (3)	C21—C16—C15	115.3 (3)
C29—C1—C15	103.0 (3)	C16—C21—C22	118.1 (3)
C14—C1—C15	112.8 (3)	C21—C22—C23	108.4 (3)
C2—C1—C15	111.5 (3)	C21—C22—C8	111.4 (3)
C7—C2—C1	115.6 (3)	C23—C22—C8	112.1 (3)
C2—C7—C8	117.9 (3)	C28—C23—C22	117.4 (3)
C9—C8—C7	108.0 (3)	C23—C28—C15	115.7 (3)
C9—C8—C22	111.4 (3)	O1—C29—O2	118.9 (3)
C7—C8—C22	112.8 (3)	O1—C29—C1	129.8 (4)
C9—C14—C1	115.1 (3)	O2—C29—C1	111.3 (3)
C30—C15—C28	111.0 (3)	C30—O2—C29	111.4 (3)
C30—C15—C16	109.8 (3)	O3—C30—O2	119.3 (3)
C28—C15—C16	109.4 (3)	O3—C30—C15	129.2 (4)
C30—C15—C1	102.8 (3)	O2—C30—C15	111.5 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
C24—H24···O3$^{\rm i}$	1.04 (3)	2.38 (3)	3.386 (5)	162 (2)

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

All H atoms were found in an electron-density difference map and their parameters were refined without constraints. The crystals, although well shaped, were rather small and poorly diffracting, so the $2\theta_{\rm max}$ value of the data collection was limited to 51°; notwithstanding this limit, the observed reflections were only 46% complete. The results are presented despite this, taking into account the fact that (I) from a chemical point of view.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *WinGX* (Version 1.64; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1561). Services for accessing these data are described at the back of the journal.

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