

8,19-Dimethyl-8,19-dihydro-8,19-ethanoanthra[2'',3'':2,3;6'',7'':2',3']di-1,4-dioxino[5,6-*b*;5',6'-*b'*]diquinoxalineBernardo Masci<sup>a\*</sup> and Pierre Thuéry<sup>b\*</sup><sup>a</sup>Dipartimento di Chimica and IMC-CNR Sezione Meccanismi di Reazione, Università 'La Sapienza', Box 34, Roma 62, P.le Aldo Moro 5, 00185 Roma, Italy, and <sup>b</sup>CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France  
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Received 22 September 2004

Accepted 30 September 2004

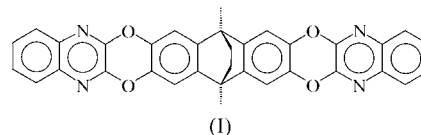
Online 31 October 2004

The title compound, C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>, results from the reaction of 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene with 2,3-dichloroquinoxaline. The molecule, which contains a binary crystallographic symmetry axis, comprises two planar 'wings' around a central bicyclic unit. The non-ideal geometry of the latter evidences some strain, as in previous compounds with the same central core. Each molecule is involved in  $\pi$ - $\pi$  interactions with four of its neighbours, oriented upside-down, which results in the formation of sheets of tightly packed molecules.

## Comment

We have previously reported the first crystal structure of a compound containing the tetrahydrodihydroethanoanthracene unit, namely 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene bis(1,4-dioxane) solvate, (II) (Masci *et al.*, 2002), as well as the structure of the octanuclear uranyl complex, (III), obtained from the corresponding tetracatecholate species (Thuéry & Masci, 2003). The compound described here, (I), is built from the same central unit.

The asymmetric unit in (I) contains half a molecule, the other half being generated by the twofold axis bisecting the



ethane bridge (Fig. 1). The dihedral angle between the two aromatic rings bound to the central curved part of the molecule is 138.88 (8)°, larger than in (II) [130.61 (4)°] and (III) [100.9 (6)°], the large deviation in (III) being due to the strain induced by uranyl coordination to form a cyclic assemblage. The dihedral angles between the same aromatic rings and the plane defined by atoms C15, C16 and their symmetry equivalents is 110.54 (9)° [114.64 (4)° in (II)]. A search of the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002) for structures containing the dihydroethanoanthracene fragment shows that these dihedral angles span very wide ranges, *viz.* 108.1–133.2° [mean value 123 (5)°] between the two aromatic rings and 110.4–131.1° [mean value 118 (4)°] between the aromatic rings and the central plane. In the simplest compound in this family, 9,10-dihydro-9,10-ethanoanthracene (or [2,3:5,6]dibenzocyclo[2.2.2]octa-2,5-diene), (IV) (Burrows *et al.*, 1999), these angles are 124.7 and 118.3° (mean value), respectively. Thus, it appears that the shape of (I) is much flatter than any other in this family of compounds. This could be an effect of the intermolecular interactions governing the packing (see below). However, larger dihedral angles between the aromatic rings are encountered in systems in which the ethane bridge is absent, for example, in compounds containing the tetramethoxydihydroanthracene fragment [151.7 (Benetollo *et al.*, 1990) and 153.3° (Guy *et al.*, 1996)].

The fused dioxine and three aromatic rings of (I) are coplanar, with an r.m.s. deviation of 0.063 Å. The maximum out-of-plane displacements are observed for atoms C4, C1 and C5 [0.145 (3), –0.091 (3) and 0.090 (3) Å, respectively]; these atoms pertain to the aromatic ring bound to the central cyclohexadiene ring, which may indicate the strain in this part of the molecule related to the rather large dihedral angle indicated above. The two O atoms are also associated with rather large out-of-plane displacements [–0.088 (3) and –0.080 (3) Å], whereas the displacements of the remaining

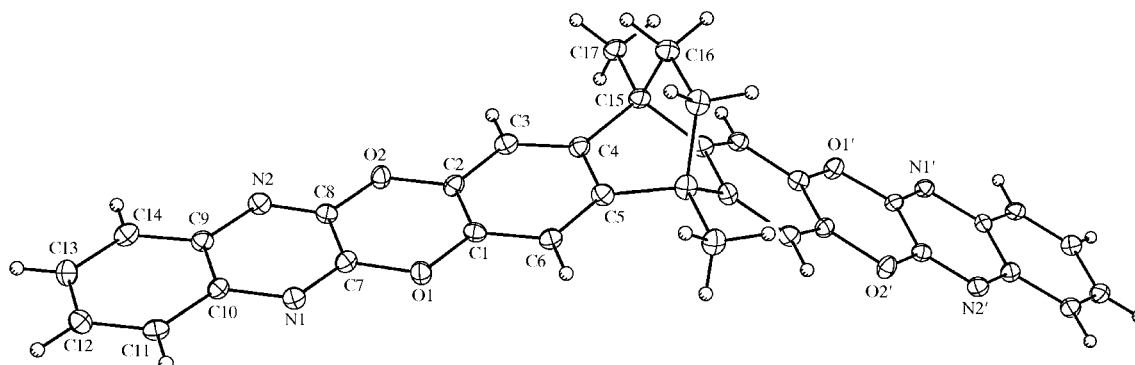


Figure 1

A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Primed atoms are at the symmetry position ( $-x, y, -\frac{1}{2} - z$ ).

atoms do not exceed 0.06 Å. The dioxine ring is nearly planar (r.m.s. deviation 0.016 Å), as is usual when it is fused to two aromatic rings. The interatomic distances in the C1–C6 aromatic ring show the same (and even more pronounced) trend as seen in (II) and (IV), with the C1–C2 bond length being shorter than C4–C5 by 0.031 Å (Table 1) [0.015 and 0.020 Å in (II) and (IV), respectively].

The bond lengths in the pyrazine ring are also somewhat irregular, with a difference of 0.029 Å between C7–C8 and C9–C10, and of 0.099 Å (mean value) between the bond lengths on each side of both N1 and N2. In the terminal aromatic ring, C9–C14, the C11–C12 and C13–C14 bond lengths are shorter than the others by 0.041 Å (mean value). In the dioxine ring, the distances around atoms O1 and O2 are also non-symmetric, with a difference of 0.025 Å (mean value). It may be noted that no other example of a compound containing such fused dioxine and pyrazine rings is present in the CSD, although the structures of three compounds with planar fused dioxine and pyridine rings have been reported (Piórko, Christie *et al.*, 1994; Piórko, Christie & Zaworotko, 1994; Troya *et al.*, 2002).

As in compounds (II) and (IV), the geometry of the central bicyclic system in (I) evidences its strained nature. The rather long C15–C16 and C16–C16' bonds are comparable with their counterparts in (II) and (IV) [primed atoms are at the symmetry position  $(-x, y, -\frac{1}{2} - z)$ ]. The 'exterior' angles C3–C4–C15 and C6–C5–C15' [mean value 125.9 (6)°] are much larger than the 'interior' angles C4–C5–C15' and C5–C4–C15 [mean value 113.9 (7)°].

The packing in (I) brings upside-down molecules into close contact, albeit slightly offset, indicating the presence of  $\pi$ – $\pi$  interactions (Fig. 2). The pyrazine ring is involved in two such contacts. One of them involves the terminal aromatic ring of the molecule related by the symmetry operation  $(\frac{1}{2} - x, -\frac{1}{2} - y, -z)$  [centroid–centroid distance = 3.590 (2) Å, mean interplanar spacing = 3.22 (2) Å, mean centroid offset = 1.59 Å, dihedral angle = 1.2° and shortest interatomic contact = 3.30 Å, which is shorter than twice the out-of-plane van der Waals radius of a C atom (1.7 Å)]. The other involves the parallel pyrazine counterpart in the neighbouring molecule at  $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$  [centroid–centroid distance = 3.673 (2) Å, interplanar spacing = 3.22 Å, centroid offset = 1.77 Å and shortest interatomic contact = 3.25 Å]. Each molecule is thus linked to four of its neighbours and infinite sheets of mol-

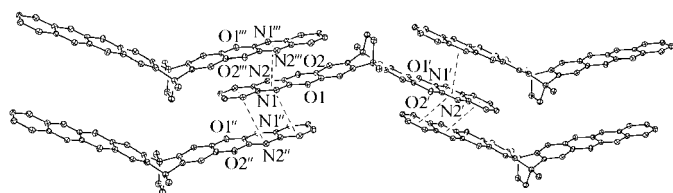


Figure 2

A partial view of the packing in (I), with the  $\pi$ – $\pi$  interactions represented as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. Primed atoms are at the symmetry position  $(-x, y, -\frac{1}{2} - z)$ , doubly primed atoms are at  $(\frac{1}{2} - x, -\frac{1}{2} - y, -z)$  and triply primed atoms are at  $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$ .

ecules parallel to the (101) plane are thus formed, successive sheets being held together by van der Waals interactions.

## Experimental

A mixture of 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene (149 mg, 0.50 mmol; Davidson & Musgrave, 1963), 2,3-dichloroquinoxaline (199 mg, 0.10 mmol) and anhydrous  $\text{Cs}_2\text{CO}_3$  (900 mg, 2.8 mmol) in acetonitrile (11 ml) was stirred and boiled under a nitrogen atmosphere for 60 h. Extraction with chloroform, followed by column chromatography on silica gel with chloroform as eluant, afforded the pure product, (I), from ethyl acetate (yield 60 mg, 22%, m.p. > 633 K).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.66 (s, 4H), 1.93 (s, 6H), 7.03 (s, 4H), 7.57 (dd, 4H,  $J = 6.0$  Hz,  $J' = 3.5$  Hz), 7.79 (dd, 4H,  $J = 6.0$  Hz,  $J' = 3.5$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  18.3, 35.4, 41.4, 110.1, 127.2, 128.8, 138.0, 139.1, 143.0, 144.9. Single crystals were obtained by slow evaporation of an ethyl acetate solution.

### Crystal data

$\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_4$   
 $M_r = 550.56$   
 Monoclinic,  $C2/c$   
 $a = 26.055$  (2) Å  
 $b = 6.6734$  (12) Å  
 $c = 14.523$  (2) Å  
 $\beta = 94.788$  (8)°  
 $V = 2516.4$  (6) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.453$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 9551 reflections  
 $\theta = 3.1$ – $25.7^\circ$   
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Needle, colourless  
 $0.15 \times 0.05 \times 0.05$  mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  scans  
 9551 measured reflections  
 2358 independent reflections  
 1196 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.075$   
 $\theta_{\text{max}} = 25.7^\circ$   
 $h = -31 \rightarrow 31$   
 $k = -8 \rightarrow 0$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.064$   
 $wR(F^2) = 0.167$   
 $S = 1.03$   
 2358 reflections  
 191 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 0.367P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.395 (4)	C6–C1	1.385 (4)
O1–C7	1.364 (4)	C4–C15	1.523 (4)
O2–C2	1.395 (4)	C5–C15 <sup>i</sup>	1.519 (4)
O2–C8	1.375 (4)	C7–C8	1.442 (5)
N1–C7	1.286 (4)	C9–C10	1.413 (5)
N1–C10	1.380 (4)	C10–C11	1.408 (4)
N2–C8	1.278 (4)	C11–C12	1.372 (4)
N2–C9	1.382 (4)	C12–C13	1.413 (5)
C1–C2	1.379 (4)	C13–C14	1.370 (5)
C2–C3	1.389 (4)	C14–C9	1.412 (4)
C3–C4	1.386 (5)	C15–C16	1.563 (5)
C4–C5	1.410 (5)	C15–C17	1.533 (5)
C5–C6	1.381 (4)	C16–C16 <sup>i</sup>	1.553 (7)
C3–C4–C15	126.3 (3)	C4–C15–C5 <sup>i</sup>	107.9 (3)
C5–C4–C15	113.9 (3)	C4–C15–C16	104.6 (3)
C6–C5–C15 <sup>i</sup>	125.5 (3)	C5 <sup>i</sup> –C15–C16	105.6 (3)
C4–C5–C15 <sup>i</sup>	113.8 (3)	C16 <sup>i</sup> –C16–C15	110.31 (17)

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

All H atoms were introduced in calculated positions as riding, with C–H = 0.93 (CH), 0.97 (CH<sub>2</sub>) and 0.96 Å (CH<sub>3</sub>), and with  $U_{\text{iso}}(\text{H}) = 1.2$  (CH or CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times  $U_{\text{eq}}(\text{C})$ .

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement and data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1027). Services for accessing these data are described at the back of the journal.

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