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7-Methoxyanthra[1,9-*de*]-1,3,2-dioxathiine-8,11-dione 2,2-dioxide

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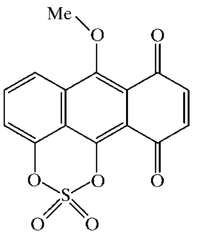
The title compound, $C_{15}H_8O_7S$, contains the first structurally characterized example of a cyclic sulfate grouping fused to an aromatic ring system.

Comment

The title compound, (I), was prepared as an intermediate in the synthesis of carminomycinone systems (Cameron *et al.*, 1989, and associated unpublished work). It is an unusual example of a cyclic sulfate system fused to an aromatic array, and as such was considered worthy of structural confirmation and definition, as described here.



(I)

The results of the room-temperature single-crystal X-ray study are consistent in terms of stoichiometry and connectivity with the formulation proposed (Fig. 1). The fused C_{14} carbocyclic ring system is essentially planar ($\chi^2 = 2170$; Fig. 2). The molecules are stacked normal to the *bc* cell diagonal, with the methoxy methyl group projecting normal to the plane, presumably a consequence of the steric demands of atoms H6 and O8, which lie on opposite faces of the molecule; the S atom lies out of the plane by 0.637 (2) Å.

The geometry of the anthracenoid carbocyclic array in (I) (Table 1) can be compared with that of a precise determination of the unsubstituted parent 1,4-anthraquinone (polymorph 1), also at room temperature (Dzyabchenko & Zavodnik, 1984), and the corresponding bond lengths and angles are generally very similar. In the quinonoid ring, the asymmetries in the exocyclic angles at atoms C8 and C11 are consistent, suggesting that these asymmetries originate not in steric interactions with the substituents at atoms C1 and C7, but rather in the increased C7a—C11a separation compared with C9—C10; the latter is a typical double bond and the former is greater than 1.427 (4) Å in both compounds. Disparities are observed in the C1—C1a—C3—C4 string, in the associated angles rather than the distances, presumably because of the introduction of substituents at atoms C1 and C3; the angles at these atoms (C11a—C1—C1a and C1a—C3—C4) are slightly larger in (I), and the C1—C1a—C3 angle is slightly smaller. In both compounds, the C7—C7a and C1—C11a distances are well below 1.40 Å, with all distances in the C1—C1a—C6a—C7 string being above that value. In the non-quinonoid peripheral ring, the distances in the C3—C1a—C6a—C6 string are all above 1.40 Å, and those in the C3–C6 string are close to or below that value, with considerable double-bond character in the C3—C4 and C5—C6 bonds, typical of naphthalene-type bond fixation.

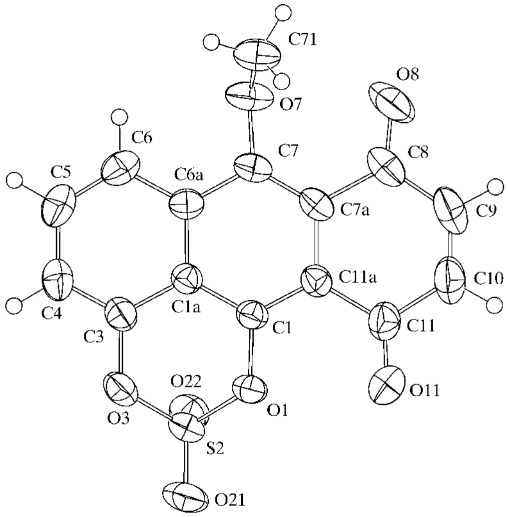


Figure 1
A projection of a single molecule of (I) normal to the aromatic plane. Displacement ellipsoids are shown at the 20% probability level for non-H atoms and H atoms are shown as spheres of arbitrary radii (0.1 Å).

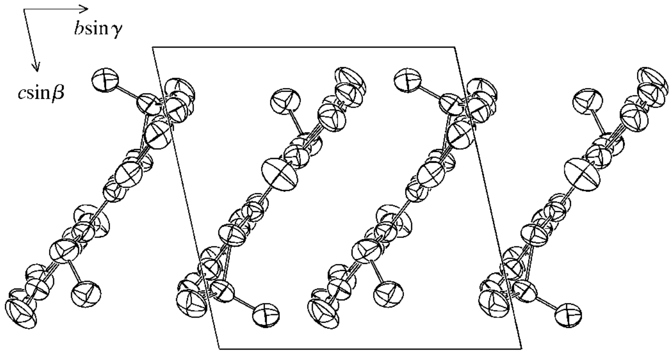


Figure 2
The unit cell projected along *a* (H atoms have been omitted), showing the crystal packing.

The sulfate ring is essentially symmetrical about the quasi-mirror plane containing atoms C1a, S, O21 and O22; the angles at the C and O atoms are all greater than 116°, but the only O—S—O angle is just 101.15 (8)°, compensated by a greatly enlarged O21—S2—O22 angle between the two short S—O bonds. Torsion angles are given in Table 1. Compound (I) is the first example of a sulfate substituting a pair of aromatic sites, although there are a limited number of other examples of systems incorporating rigid support of other types. Nevertheless, O···O distances bridged by simple $(CH_2)_n$ (n = 2, 3 or 4) polymethylene sequences, *viz.* 2.322 (7), 2.421 (3), 2.415 (3) and 2.427(3) Å, respectively (Boer *et al.*, 1968; Lowe *et al.*, 1988; Krüger *et al.*, 1998), suggest the present value [O1···O3 = 2.433 (2) Å] to be relatively unstrained.

Experimental

The synthesis of the title compound is described by Cameron *et al.* (1989). Crystals (m.p. 483–486 K) were obtained from light petroleum. Analysis found: C 54.2, H 2.5, S 9.7%; $C_{15}H_8O_7S$ requires: C 54.2, H 2.4, S 9.6%. λ_{max} (log ε): 236, 283 (*sh*), 295 (*sh*), 330 (*sh*), 415 nm (4.70, 3.82, 3.80, 3.47, 3.71); IR (cm^{-1}): ν_{max} 1660, 1618; ^{1}H NMR: δ 4.10 (*s*, OCH_3), 6.98 (*s*, H9, H10), 7.50 (*dd*, J = 8, 1 Hz, H4), 7.84 (*t*, J = 8 Hz, H5), 8.31 (*dd*, J = 8, 1 Hz, H6); m/z 332 (M^+, 100%).

Crystal data

$C_{15}H_8O_7S$
M_r = 332.29
Triclinic, $P\overline{1}$
a = 9.359 (2) Å
b = 9.406 (2) Å
c = 9.509 (2) Å
α = 68.05 (2)°
β = 64.17 (2)°
γ = 62.580 (10)°
V = 652.9 (3) Å^3

Z = 2
D_x = 1.69 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6 reflections
θ = 19.8–21.1°
μ = 0.29 mm^{-1}
T = 293 (2) K
Block, colourless
0.42 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
2θ–ω scans
4485 measured reflections
4485 independent reflections
3316 reflections with $I > 3\sigma(I)$
θ_{max} = 32.5°

h = 0 → 14
k = −12 → 14
l = −12 → 12
6 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.046
wR = 0.058
S = 1.08
3316 reflections
208 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.0003F^2]$, where $\sigma(I) = [\sigma(I)_{meas} + 0.0004(I_{net})^2]^{1/2}$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

H atoms were found in difference Fourier maps and were placed at idealized positions [C—H = 0.95 Å, U_{iso}(H) = 1.25U_{eq}(C) for CH and 1.5U_{eq}(C) for CH_3] and not refined.

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.404 (3)	C6a—C7	1.428 (2)
C1—C1a	1.408 (3)	C7—O7	1.356 (3)
C1—C11a	1.369 (2)	C7—C7a	1.380 (3)
O1—S2	1.5759 (14)	O7—C71	1.431 (3)
S2—O21	1.405 (3)	C7a—C8	1.493 (2)
S2—O22	1.403 (2)	C7a—C11a	1.443 (3)
S2—O3	1.5741 (17)	C8—O8	1.217 (4)
C1a—C3	1.410 (2)	C8—C9	1.468 (5)
C1a—C6a	1.410 (3)	C9—C10	1.314 (5)
C3—O3	1.414 (3)	C10—C11	1.461 (3)
C3—C4	1.356 (4)	C11—O11	1.212 (4)
C5—C6	1.366 (3)	C11—C11a	1.492 (4)
C6—C6a	1.418 (4)		
O1—C1—C1a	117.06 (14)	O22—S2—O3	109.64 (12)
O1—C1—C11a	119.7 (2)	C1—C1a—C3	122.8 (2)
C1a—C1—C11a	123.2 (2)	C1—C1a—C6a	119.18 (15)
C1—O1—S2	117.08 (17)	C3—C1a—C6a	118.0 (2)
O1—S2—O21	105.98 (12)	C1a—C3—O3	118.5 (2)
O1—S2—O22	109.70 (9)	C1a—C3—C4	123.2 (2)
O1—S2—O3	101.15 (8)	O3—C3—C4	118.23 (17)
O21—S2—O22	122.14 (10)	S2—O3—C3	116.04 (11)
O21—S2—O3	106.17 (10)	C3—C4—C5	117.9 (2)
C1a—C1—O1—S2	33.7 (2)	O1—S2—O3—C3	53.3 (2)
O1—C1—C1a—C3	−3.3 (3)	C1—C1a—C3—O3	2.1 (3)
C1—O1—S2—O3	−55.41 (14)	C1a—C3—O3—S2	−31.0 (3)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1278). Services for accessing these data are described at the back of the journal.

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