tory, managed by Lockheed Martin Energy Research Corporation. This research was supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute for Science and Education and Oak Ridge National Laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1447). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Bryan, J. C., Lavis, J. M. & Sachleben, R. A. (1998). *Acta Cryst.* C**54**, 1662–1666.
Burns, J. H., Bryan, J. C., Davis, M. C. & Sachleben, R. A. (1996). *J. Incl. Phenom. Mol. Recognit. Chem.* **26**, 197–207.
Enraf–Nonius (1993). *CAD-4-PC Software*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
Harms, K. (1995). *XCAD4. Program for the Lp Correction of Enraf–Nonius Four-Circle Diffractometer Data*. University of Marburg, Germany.
Sachleben, R. A., Deng, Y. & Moyer, B. A. (1996). *Solvent Extr. Ion Exch.* **14**, 995–1015.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1995). *SHELXTL*. Version 5.03/IRIX. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1998). *PLATON. A Multi-Purpose Crystallographic Tool*. University of Utrecht, The Netherlands.
Vögtle, F. & Weber, E. (1992). *J. Incl. Phenom. Mol. Recognit. Chem.* **12**, 75–119.

Acta Cryst. (1999). C**55**, 620–622

A new strained angularly fused ring system: 8-hydroxy-1,2,3-trimethoxybenz[*a*]-anthracene-7,12-dione

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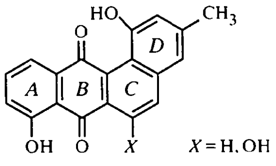
(*Received 21 July 1998; accepted 5 October 1998*)

Abstract

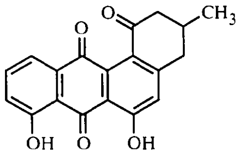
The synthesis and crystal structure of the title compound ($C_{21}H_{16}O_6$) are reported. The introduction of a methoxy group at the 1-position brings two O atoms into close proximity with an O···O separation of 2.611 (3) Å. This interaction causes severe deformation of ring *B* but not ring *D*.

Comment

Recently, natural product researchers have determined the structures of tetracyclic aromatic compounds which are angularly fused. Some of these quinones, such as (1) and (2), exhibit significant activity (Rohr & Thiercke, 1992). Total syntheses have been recorded (Krohn, 1990). In our pathway, the angularly fused ring system was assembled by a strategy which is dramatically different from the previously reported pathways. Our original synthetic approach to this class of compounds will be published elsewhere.

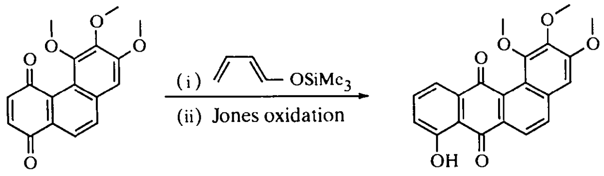


(1)



(2)

The reaction of (3) with 1-(trimethylsilyloxy)-1,3-butadiene in methylene chloride followed by Jones oxidation provided a single product in 84% yield which was characterized by ^{1}H and ^{13}C NMR spectroscopy. However, the position of the hydroxyl group remained unclear. To confirm the expected regioselectivity, the X-ray structural analysis of (4) was performed.



(3) (4)

It is obvious from Fig. 1 and planarity calculations that the close proximity of atoms O1 and O6 introduces significant strain in the molecule. The strain is somewhat relieved by the subsequent deformation of the molecule, resulting in the excursion of atoms O1 and O6 to opposite sides of the plane defined by C1, C18, C17, and C16. The O1···O6 distance is 2.611 (3) Å, which is considerably smaller than the van der Waals separation of 3.02 Å (Bott *et al.*, 1980) and somewhat shorter than the corresponding O···O distance [average 2.534 (10) Å] reported for 4,5-dimethoxyphenanthrene, (5) (Cosmo *et al.*, 1990)

One measure of strain is the distance between atoms C3 and C4, and C9 and C10. In strained 4,5-disubstituted phenanthrenes, the relevant distances are in the range 1.452 (6)–1.469 (6) Å (Cosmo *et al.*, 1990), while in (4), C3—C4 and C9—C10 are 1.369 (3) and 1.455 (3) Å, respectively. Another measure of strain is the sum of the squares of the deviations from planarity through rings *D* and *B*. These sums were found to be

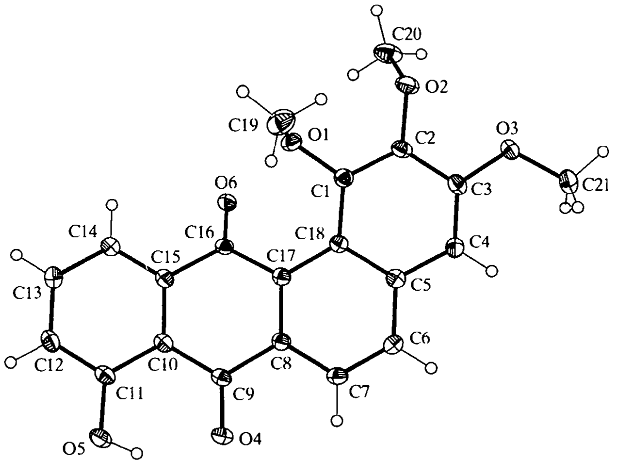


Fig. 1. Molecular structure of (4). The displacement ellipsoids are shown at the 30% probability level.

0.007 and 0.050 Å^2 for rings *D* and *B*, respectively. The corresponding values in (5) averaged ~0.014 Å^2.

Thus, according to the two approaches, the strain imposed on the fused ring system is relieved mainly by the severe deformation of the quinone ring and expulsion of atoms C16 and O6 out of the anthracene plane, while ring *D* remains virtually planar. This is not unexpected because ring *B* is not aromatic while ring *D* is part of a conjugated π-system. The twist of the phenanthrene and anthracene moieties can be estimated by the torsion angles C1—C18—C17—C16 and C18—C17—C16—O6 which are 25.0 (3) and 24.4 (3)°, respectively.

While in many methoxy-substituted phenyl rings both C and O atoms of the methoxy group lie in the plane of the ring owing to delocalization of the π-electrons into the C(phenyl)—O bond, two out of three methoxy-C atoms in (4) are out of the plane of the phenyl ring. Their mutual location corresponds to the energetically most favorable conformation. C21 is coplanar with ring *D* within 0.006 Å while the torsion angle C21—O2—C2—C4 is −3.8 (3)°. The shortest interactions between the methyl group and atoms C4 and H4*A* span over 2.822 (4) (C—C), 2.528–2.789 (4) Å (C—H) and 2.292–2.349 (4) Å (H—H) and compare well with the analogous distances in (5). These interactions result in the opening of angle C4—C3—O3 to 125.7 (2)° and closing of O3—C3—C2 to 114.5 (2)°. These values are also in good agreement with the angles reported for (5). The C—OCH$_3$ bonds in (4) [average 1.367 (2) Å] are almost identical to that found in (5) [1.360 (3) Å] but appreciably shorter than the average H$_3$C—O distance [1.427 (3) in (4) and 1.406 (5) Å in (5)]. This fact confirms the multiple character of the C3—O3 bond and the existence of a substantial electronic rotation barrier that prevents tilting of the methyl group despite its strong interactions with atoms C4 and H4*A*. Atoms C20 and C19 reside on opposite sides of the plane defined by atoms O1, C1, C2, and O2 to avoid an unfavorable interaction between the methyl-C atoms. The torsion angles C19—O1—C1—C2 and C20—O2—C2—C1 are −78.1 (3) and −77.6 (3)°, respectively.

Experimental

8-Hydroxy-1,2,3-trimethoxybenz[*a*]anthracene-7,12-dione was prepared by adding a stirred solution of 5,6,7-trimethoxy-1,4-phenanthrenequinone (58.4 mg, 0.2 mmol) in dry methylene chloride (5 ml) under argon at 195 K to 1-(trimethylsilyloxy)-1,3-butadiene (0.14 ml, 0.8 mmol) and the resulting solution was allowed to warm up slowly to room temperature. Volatiles were removed under reduced pressure and the residue was dissolved in acetone (5 ml) and treated with a 2.7 *M* solution of Jones reagent (0.163 ml, 0.44 mmol) at 273 K. After 1 h, 10 drops of 2-propanol were added and the reaction mixture was partitioned between chloroform and water. The aqueous layer was extracted with chloroform, and the combined organic fractions were washed with water and brine and dried over MgSO$_4$. The solvent was removed and the residue purified by silica gel chromatography (elution with 20% ethyl acetate in hexane) to afford 61 mg (84%) of the title compound as a red solid. X-ray quality crystals were obtained by slow crystallization from hexane/benzene. ^{1}H NMR (CDCl$_3$, 295 K, δ) 3.98 (*s*, 1H), 4.03 (*s*, 6H), 6.99 (*s*, 1H), 7.23 (*dd*, J = 1.8, 7.2 Hz, 1H), 7.58–7.66 (*m*, 2H), 7.90 (*d*, J = 8.7 Hz, 1H), 8.16 (*d*, J = 8.7 Hz, 1H), 12.24 (*s*, 1H); ^{13}C (CDCl$_3$, 295 K, δ) 56.2, 61.1, 61.3, 102.9, 115.6, 118.2, 120.8, 121.5, 122.7, 131.8, 132.1, 135.2, 136.6, 136.7, 137.1, 143.9, 150.7, 156.2, 161.6, 185.9, 188.3.

Crystal data

$C_{21}H_{16}O_6$
M_r = 364.34
Triclinic
$P\overline{1}$
a = 7.5766 (6) Å
b = 9.6207 (7) Å
c = 11.2537 (9) Å
α = 89.227 (1)°
β = 85.764 (1)°
γ = 82.531 (1)°
V = 811.12 (11) Å^3
Z = 2
D_x = 1.492 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 68 reflections
θ = 8–23°
μ = 0.110 mm^{-1}
T = 173 (2) K
Block
0.40 × 0.30 × 0.20 mm
Red

Data collection

Bruker CCD-1000 area-detector diffractometer
φ scans
Absorption correction: none
6385 measured reflections
3260 independent reflections

2652 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\max}$ = 26.41°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.163

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.3126P]$ where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.05$
3260 reflections
244 parameters
H atoms treated by a mixture of independent and constrained refinement

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *SMART* (Bruker, 1996). Cell refinement: *SMART*. Data reduction: *SHELXTL* (Sheldrick, 1997). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1433). Services for accessing these data are described at the back of the journal.

References

Bott, G., Field, L. D. & Sternhell, S. (1980). *J. Am. Chem. Soc.* **102**, 5618–5626.

Bruker (1996). *SMART Software Reference Manual*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Cosmo, R., Hambley, T. W. & Sternhell, S. (1990). *Acta Cryst.* B**46**, 557–562.

Krohn, K. (1990). *Tetrahedron*, **46**, 291–318.

Rohr, J. & Thiercke, R. (1992). *Nat. Prod. Rep.* **9**, 103–137.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.03. *Reference Manual*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 622–624

Spiro[1-azabicyclo[5.3.0]decane-6,2′(5′*H*)-furan]-5′,10-dione: an example of kryptoracemic crystallization

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(*Received 28 April 1998; accepted 2 October 1998*)

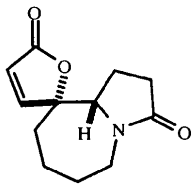
Abstract

A racemic mixture of the title compound, $C_{12}H_{15}NO_3$, crystallizes in the chiral, monoclinic space group $P2_1$, with one enantiomerically related pair of molecules per asymmetric unit. This mode of crystallization is extremely rare. The molecules pack to form several close C—H···O interactions. Interestingly, while the conformations of the individual rings in the two molecules are very similar, the overall molecular conformation is different.

Comment

Kryptoracemic crystallization, a term coined by Bernal *et al.* (1996), describes the phenomenon of a racemate crystallizing into a chiral space group where the contents of the asymmetric unit constitute a racemic mixture. Kryptoracemic crystallization is similar to conglomerate crystallization in that a racemic compound forms chiral crystals. However, in conglomerate crystallization, which has been estimated to occur with a frequency of 5–10% (Jacques *et al.*, 1981), the racemate spontaneously resolves into a mixture of crystals of the pure enantiomers. Judging by the number of known examples, kryptoracemic crystallization occurs much less frequently (Bernal *et al.*, 1996). However, many of the examples of organic molecules forming kryptoracemic crystals identified by Bernal *et al.* (1996) were incorrectly characterized as such. Those that are true kryptoracemates are reported by Furberg & Hassel (1950), Mostad *et al.* (1975), Schouwstra (1973), Baert *et al.* (1978), Bigoli *et al.* (1981) and Furusaki *et al.* (1982).

In the title compound, (I), molecules of alternating chirality stack in columns along the *c* axis. Within a column, molecules are connected by a series of C—H···O hydrogen bonds. Adjacent columns related by an *a*-axis translation are also hydrogen-bonded resulting in a two-dimensional C—H···O hydrogen-bonding network perpendicular to the *b* axis. Three of



(I)

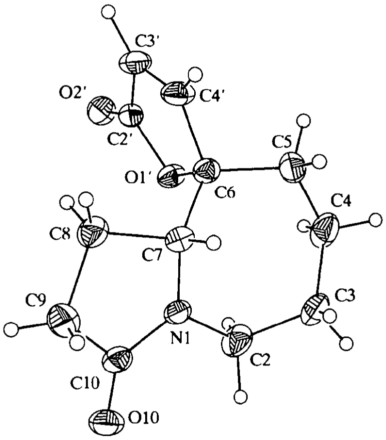


Fig. 1. View of molecule 1 showing the atom-labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. H atoms are drawn to an arbitrary scale.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999