

Table 3. Hydrogen bonds (Å, °) and possible hydrogen bonds (Å)

D—H...A	D—H	H...A	D...A	D—H—A	Symmetry
O(1)—H(O1)...O(4)	0.80 (4)	2.40 (4)	3.163 (4)	160 (3)	<i>x,y,z</i>
O(2)—H(O2)...O(3)	1.01 (3)	2.02 (4)	2.955 (4)	153 (3)	<i>x,y,z</i>
N(2)—H(O3)...O(5)	1.05 (4)	1.94 (4)	2.927 (5)	155 (3)	1- <i>x</i> , -0.5 + <i>y</i> , 1.5 - <i>z</i>
D...A	D...A	Symmetry			
O(3)...O(4)	3.001 (4)	<i>x,y,z</i>			
O(3)...N(1)	2.913 (4)	<i>x,y,z</i>			
O(4)...O(5)	3.173 (6)	<i>x,y,z</i>			
O(4)...O(6)	3.035 (6)	<i>x,y,z</i>			
O(4)...N(3)	2.792 (4)	<i>x,y,z</i>			
O(5)...O(6)	2.925 (7)	1.0 - <i>x</i> , 1.0 - <i>y</i> , 1.0 - <i>z</i>			
O(6)...O(7)	2.901 (9)	<i>x,y,z</i>			
O(7)...O(1)	2.839 (5)	<i>x,y,z</i>			
O(7)...O(7')	3.031 (8)	1.0 - <i>x</i> , - <i>y</i> , 1.0 - <i>z</i>			
O(7)...O(8)	2.64 (3)	<i>x,y,z</i>			

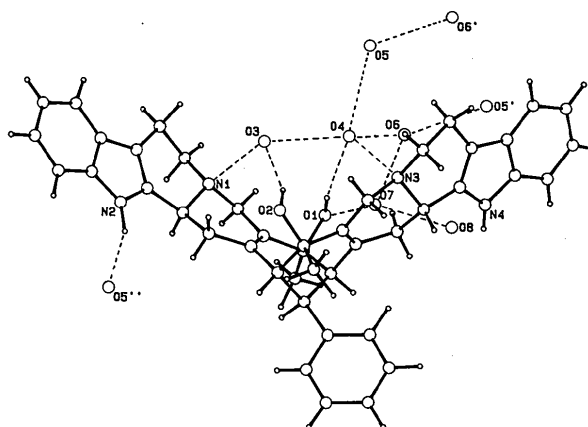


Fig. 2. View of the molecule showing the hydrophilic cavity and the hydrogen-bond network.

bonds differ by less than 5°. Only the different substituents at C(9) lead to a local deviation of the molecular symmetry from *C*₂.

The overall shape of the rigid molecule is that of a V-shaped propeller. The V shape of the molecule is a consequence of the conformation of the bicyclo-[3.3.1]nona-2,6-diene group which has the conformation characteristic for this group (Radcliffe, Gutierrez, Blount & Mislow, 1984; Quast, Görlach, Stawitz, Peters, Peters & von Schnering, 1984).

The concave side of the molecule encloses a hydrophilic cavity (Fig. 2) flanked by the hydroxyl groups O(1) and O(2) and the pyramidal amine atoms N(1) and N(3). This cavity contains the hydrate molecules O(3) and O(4) which are tightly connected to the main molecule by a network of hydrogen bonds (Table 3). The hydrate molecules O(5), O(6) and O(7) form a second hydration sphere and contribute to the intermolecular bonding *via* a hydrogen bond between O(5) and the amino group N(2) of a neighboring molecule. The amino group N(4) is not involved in hydrogen bonding.

The partly occupied water molecule represented by O(8) has a contact distance of 2.64 (3) Å to O(7) indicating a possible hydrogen bond. However, O(8) has no other contact distances short enough for hydrogen bonding. Thus O(8) mainly serves space-filling purposes and does not contribute to the intermolecular bonding.

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Spiro[1,3-benzodioxole-2,9'(10'*H*)-phenanthren]-10'-one

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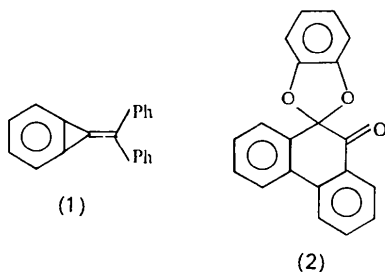
Abstract. C₂₀H₁₂O₃, *M_r* = 300.3, triclinic, *P* $\bar{1}$, *a* = 699.9 (7) Å³, *Z* = 2, *D_x* = 1.42 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.104 mm⁻¹, *F*(000) = 312, *T* = 69.10 (5), β = 72.31 (4), γ = 72.14 (4)°, *V* = 133 K, *R* = 0.072 for 581 unique observed reflections.

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The planar 1,3-benzodioxole moiety deviates from a bisecting position with respect to the two phenanthrene aromatic rings, which are in turn twisted 9° from coplanarity. The variation of bond lengths around the central C(2)(9') carbon atom, similar to that found in grandidone D, suggests a structural compromise between intermolecular contacts and resonance-bonding requirements.

Introduction. The preparations of a range of stable hydrocarbons with structures based upon the fusion of a methylenecyclopropene into an aromatic ring, e.g. (1), have been reported (Halton, Randall, Gainsford & Stang, 1986) and reviewed (Halton & Stang, 1987) and the behaviour of representative examples towards electrophiles (Buckland, Halton, Mei & Stang, 1987) as well as nucleophiles and oxidizing agents (Buckland, Halton & Stang, 1988) has been examined. In this last study it was found that the diphenylmethylenecyclopropabenzene (1) reacts much more rapidly with singlet oxygen and provides a more complex product mixture than does its cyclopropa[b]naphthalene homologue. The title compound (2) was the only product isolated from reaction of (1) with singlet oxygen, in low (13%) yield.



Experimental. A yellow needle-like crystal, $0.09 \times 0.14 \times 0.30$ mm, was mounted on a glass fibre in random orientation on a Nicolet R3m computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator [$\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$]. Cell dimensions were determined using 17 reflections, $5.4 < 2\theta < 17^\circ$, and a total of 2858 reflections ($h, \pm k, \pm l$) including standards were measured within the limits $4 < 2\theta < 50^\circ$ at 133 K using ω scans of 2.6° . Equivalent reflections were averaged and the 581 reflections (h 0 to 9, k -11 to 11, l -14 to 14) with intensities 3.0 times their standard deviations (from counting statistics) were corrected for Lorentz and polarization factors. As the intensities of standards dropped uniformly over the data collection by an average of 16%, rescaling was applied using their averaged values. No absorption correction was applied.

Structure solution was by direct methods (SHELXTL; Sheldrick, 1984) and successive

difference Fourier syntheses. Hydrogen atoms were not located, but included in calculated positions (C—H 0.95 \AA). Refinement (SHELX76; Sheldrick, 1976) was by weighted full-matrix least squares minimizing $w\Delta^2$, where $\Delta = |F_o| - |F_c|$, $w = [\sigma(F_o)^2 + 0.0005F_o^2]^{-2}$ and F_o, F_c are the observed and calculated structure factors, respectively. One common isotropic thermal parameter was refined for all hydrogen atoms. Atoms C(3') and C(6) were refined with isotropic thermal parameters; all other atoms were refined with anisotropic thermal parameters.

Scattering factors for non-hydrogen and hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Stewart, Davidson & Simpson (1965). The final cycle included 199 variables, and converged (maximum $\Delta/\sigma = 0.16$) with $R = 0.072$, $wR = 0.074$. No correlation coefficients were greater than 0.50. In the final difference Fourier synthesis $\Delta\rho$ max. = 0.34 and min. = -0.32 e \AA^{-3} . The program ORTEP (Johnson, 1971) as implemented in the GX package (Gilmore, Mallinson & Muir, 1985) was used to produce views of the molecule.

Discussion. Final positional and equivalent isotropic parameters of (2) are shown in Table 1, and bond lengths, bond angles and selected torsion angles are shown in Table 2.* The molecule and numbering scheme are shown in Fig. 1.

The structure consists of independent molecules of (2), with only van der Waals intermolecular interactions; the closest contacts for H...H and O...H are ≥ 2.33 and 2.70 \AA , respectively. The torsion-angle and mean-plane calculations confirm that the benzene rings of the phenanthrene segment are each planar, but twisted from mutual coplanarity by 9° . The benzodioxole moiety is also planar, making angles of 97 and 77° with the phenanthrene benzene rings (see Fig. 2). Atoms C(10') and O(11') deviate from the plane of the closest benzene ring by 0.044 and 0.241 \AA , respectively.

Comparison with the structure of grandidone D (Uchida, Miyase, Yoshizaki, Bieri, Ruedi & Eugster, 1981) (hereafter GND) shows many similarities in the bonding-distance variations around the 'link' atom C(2): the GND value appears first in the following discussions. In both structures, the distances C(2)—O(1) and C(2)—O(3) are consistently different from each other: [1.48 (1), 1.49 (2) and 1.40 (1), 1.44 (2) \AA], with the angle C(8a')—C(2)—C(10') opened from a tetrahedral value

* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53089 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters for non-hydrogen atoms and their e.s.d.'s

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^3$)
O(1)	0.1555 (17)	0.1537 (11)	0.2539 (10)	3.1 (4)
O(3)	0.4418 (17)	0.1358 (11)	0.2888 (10)	3.2 (5)
O(11')	0.2011 (19)	0.3661 (11)	0.3959 (10)	4.1 (5)
C(2)	0.3002 (27)	0.2444 (17)	0.2233 (15)	2.8 (5)
C(3a)	0.2098 (27)	0.0053 (19)	0.3435 (13)	2.8 (5)
C(4)	0.1222 (29)	-0.1200 (15)	0.4014 (13)	3.7 (5)
C(5)	0.2122 (27)	-0.2599 (16)	0.4837 (13)	3.8 (5)
C(6)	0.3736 (29)	-0.2720 (21)	0.5044 (16)	3.8 (5)†
C(7)	0.4669 (26)	-0.1429 (16)	0.4435 (13)	3.5 (5)
C(7a)	0.3726 (26)	-0.0054 (15)	0.3644 (13)	2.5 (5)
C(10')	0.1964 (30)	0.3879 (7)	0.2836 (15)	3.0 (5)
C(10a)	0.1091 (27)	0.5336 (17)	0.2032 (16)	2.9 (5)
C(1)	-0.0239 (25)	0.6461 (18)	0.2587 (16)	3.1 (5)
C(2')	-0.1212 (29)	0.7903 (18)	0.1838 (15)	3.9 (5)
C(3')	-0.0799 (27)	0.8166 (19)	0.0530 (15)	3.6 (5)†
C(4')	0.0519 (24)	0.7100 (17)	-0.0058 (15)	3.1 (5)
C(4a')	0.1476 (27)	0.5619 (16)	0.0680 (15)	2.4 (5)
C(4b')	0.2928 (29)	0.4439 (17)	0.0079 (13)	3.1 (6)
C(5')	0.3576 (25)	0.4831 (16)	-0.1252 (13)	2.2 (5)
C(6')	0.4915 (24)	0.3752 (18)	-0.1850 (15)	3.0 (5)
C(7')	0.5695 (27)	0.2249 (18)	-0.1066 (15)	3.6 (6)
C(8')	0.5114 (30)	0.1849 (17)	0.0243 (15)	3.3 (5)
C(8a')	0.3713 (27)	0.2943 (17)	0.0823 (13)	1.9 (5)

† Refined isotropically.

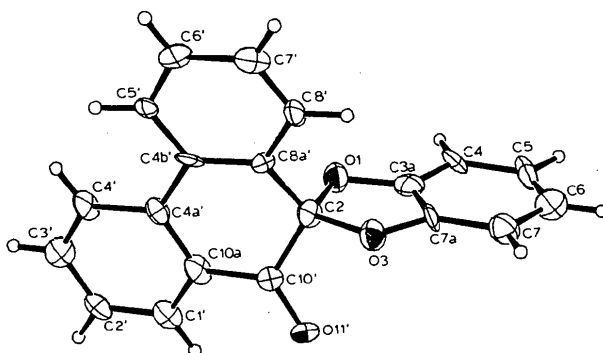


Fig. 1. Computer-generated diagram (Johnson, 1971) illustrating the molecule and the atom-labelling scheme with 50% probability ellipsoids.

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$)

O(1)—C(2)	1.49 (2)	O(1)—C(3a)	1.39 (2)
O(3)—C(2)	1.44 (2)	O(3)—C(7a)	1.41 (2)
O(11')—C(10')	1.24 (2)	C(2)—C(10')	1.56 (2)
C(2)—C(8a')	1.48 (2)	C(3a)—C(4)	1.36 (2)
C(3a)—C(7a)	1.35 (2)	C(4)—C(5)	1.41 (2)
C(5)—C(6)	1.33 (2)	C(6)—C(7)	1.41 (2)
C(7)—C(7a)	1.39 (2)	C(10')—C(10a)	1.41 (2)
C(10a)—C(1')	1.39 (2)	C(10a)—C(4a')	1.42 (2)
C(1)—C(2')	1.41 (2)	C(2')—C(3')	1.37 (2)
C(3')—C(4')	1.37 (2)	C(4')—C(4a')	1.42 (2)
C(4a')—C(4b')	1.48 (2)	C(4b')—C(5')	1.40 (3)
C(4b')—C(8a')	1.38 (2)	C(5')—C(6')	1.39 (2)
C(6')—C(7')	1.40 (2)	C(7')—C(8')	1.37 (2)
C(8)—C(8a')	1.41 (2)		
C(3a)—O(1)—C(2)	105 (1)	C(7a)—O(3)—C(2)	105 (1)
O(3)—C(2)—O(1)	108 (1)	C(10')—C(2)—O(1)	102 (2)
C(10')—C(2)—O(3)	111 (1)	C(8a')—C(2)—O(1)	109 (1)
C(8a')—C(2)—O(3)	111 (2)	C(8a')—C(2)—C(10')	115 (1)
C(4)—C(3a)—O(1)	128 (2)	C(7a)—C(3a)—O(1)	111 (2)
C(7a)—C(3a)—C(4)	122 (2)	C(5)—C(4)—C(3a)	116 (2)
C(6)—C(5)—C(4)	123 (2)	C(7)—C(6)—C(5)	122 (2)
C(7a)—C(7)—C(6)	114 (2)	C(3a)—C(7a)—O(3)	112 (1)
C(7)—C(7a)—O(3)	124 (2)	C(7)—C(7a)—C(3a)	124 (2)
C(2)—C(10')—O(11')	118 (2)	C(10a)—C(10')—O(11')	126 (2)
C(10a)—C(10')—C(2)	117 (1)	C(1')—C(10a)—C(10')	119 (2)
C(4a')—C(10a)—C(10')	121 (2)	C(4a')—C(10a)—C(1')	120 (2)
C(2')—C(1')—C(10a)	122 (2)	C(3')—C(2')—C(1')	118 (2)
C(4')—C(3')—C(2')	123 (2)	C(4a')—C(4')—C(3')	121 (2)
C(4')—C(4a')—C(10a)	118 (2)	C(4b')—C(4a')—C(10a)	120 (2)
C(4b')—C(4a')—C(4')	122 (2)	C(5')—C(4b')—C(4a')	121 (1)
C(8a')—C(4b')—C(4a')	121 (2)	C(8a')—C(4b')—C(5')	118 (2)
C(6')—C(5')—C(4b')	123 (1)	C(7')—C(6')—C(5')	118 (2)
C(8')—C(7')—C(6')	121 (2)	C(8a')—C(8')—C(7')	120 (2)
C(4b')—C(8a')—C(2)	120 (2)	C(8')—C(8a')—C(2)	120 (1)
C(8')—C(8a')—C(4b')	120 (1)		
C(3a)—O(1)—C(2)—O(3)	5	C(3a)—O(1)—C(2)—C(10')	-111
C(3a)—O(1)—C(2)—C(8')	126	C(2)—O(1)—C(3a)—C(4)	180
C(2)—O(1)—C(3a)—C(7a)	-3	C(7a)—O(3)—C(2)—O(1)	-6
C(7a)—O(3)—C(2)—C(10')	105	C(7a)—O(3)—C(2)—C(8a')	-124
C(2)—O(3)—C(7a)—C(10')	4	C(2)—O(3)—C(7a)—C(7)	180
O(1)—C(2)—C(10')—O(11')	92	O(1)—O(2)—C(10')—C(10a)	-90
O(3)—C(2)—C(10')—O(11')	-23	O(3)—C(2)—C(10')—C(10a)	155
C(8a')—C(2)—C(10')—O(11')	-150	C(8a')—C(2)—C(10')—C(10a)	28
O(1)—C(2)—C(8a')—C(4b')	90	O(1)—C(2)—C(8a')—C(8')	-86
O(3)—C(2)—C(8a')—C(4b')	-151	O(3)—C(2)—C(8a')—C(8')	32
C(10')—C(2)—C(8a')—C(4b')	-24	C(10')—C(2)—C(8a')—C(8')	160
O(11')—C(10')—C(10a)—C(4a')	164	O(11')—C(10')—C(10a)—C(1')	-20
C(2)—C(10')—C(10a)—C(4a')	-14	C(2)—C(10')—C(10a)—C(1')	162
C(10')—C(10a)—C(4a')—C(4b')	-5	C(10')—C(10a)—C(1')—C(2)	-177
C(10a)—C(4a')—C(4b')—C(5')	-168	C(10a)—C(4a')—C(4b')—C(8a')	10
C(4')—C(4a')—C(4b')—C(5b)	8	C(4')—C(4a')—C(4b')—C(8a')	-174
C(4a')—C(4b')—C(5')—C(6')	-179	C(7')—C(8')—C(8a')—C(2)	175
C(4a')—C(4b')—C(8a')—C(2)	5		

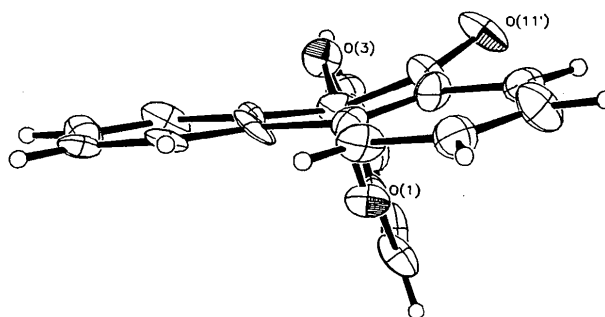


Fig. 2. View of (2) illustrating angles between ring systems.

[114.1 (6), 115 (1) $^\circ$]. The benzodioxole six-membered-ring bond distances suggest some localization of bonding in (2) [C(5)—C(6) 1.33 (2), C(6)—C(7) 1.41 (2) \AA] but are neither significant nor confirmed by comparison with GND.

The notable difference between (2) and GND relates to the twist in the planes illustrated in Fig. 2: in GND, the interplanar angle between the benzodioxole and the unsaturated (benzene-type) ring [atoms C(8)⋯C(14)] is 87 $^\circ$ (compared with 97 and 77 $^\circ$ here). Note that the other fused ring in GND is a cyclohexane type, adopting a chair conformation. It is concluded that variations in bond distance around C(2) alleviate its constrained geometry at the fusing of the three ring systems. The interplanar twists in (2) may occur because they minimize intramolecular

contacts between the carbonyl and the benzodioxole ring oxygens [O(11'), O(3)] without compromising the delocalized bonding in the phenanthrenone-benzene rings. In GND, the cyclohexane ring system is sufficiently flexible to cope with these contacts.

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Structure of 4,4,5,5-Tetramethoxy-2,7-dimethylcyclohepta-2,6-dien-1-one

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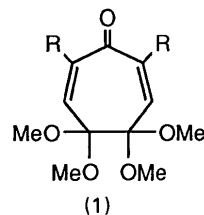
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(Received 27 April 1989; accepted 26 February 1990)

Abstract. $C_{13}H_{20}O_5$, $M_r = 256.30$, triclinic, $P\bar{1}$, $a = 7.535$ (2), $b = 9.472$ (3), $c = 10.927$ (3) Å, $\alpha = 104.631$ (3), $\beta = 103.430$ (2), $\gamma = 109.130$ (3)°, $V = 669.34$ Å³, $Z = 2$, $D_x = 1.272$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 0.91$ cm⁻¹, $F(000) = 276$, $T = 293$ K, $R = 0.045$ for 2316 observed reflections. The crystal structure has a saddle-like C_1 symmetrical conformation: the angle of intersection between the two double bonds is 148.3° and the carbonyl oxygen atom is out of the two planes of the double bonds.

Introduction. Recently, we investigated the conformational exchanges of 4,4,5,5-tetramethoxycyclohepta-2,6-dienones (1) and 6,6,7,7-tetramethoxycyclohepta-2,4-dien-1-one (2) by variable-temperature NMR spectroscopy and found that the ground-state structure of (1) has C_1 symmetry

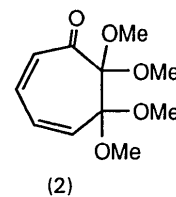
(Mori, Kubota & Takeshita, 1989). This conclusion is analogous to that for 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene derivatives (Weissensteiner, Hofer & Wagner, 1988). We report here the crystal structure of 4,4,5,5-tetramethoxy-2,7-dimethylcyclohepta-2,6-dien-1-one (1a), a monocyclic cyclohepta-2,6-dienone system.



a R = Me

b R = H

c R = 'Pr



Experimental. Crystalline (1a) was prepared as previously reported (Mori, Kubota & Takeshita, 1988)