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Structure of *cis*-9-[(Benzyloxy)methoxy]-4a,9,9a,10-tetrahydro-9,10-*o*-benzenoanthracene-1,4-dione, a Sterically Congested 2-Ene-1,4-dione

BY PARIMAL BHARADWAJ, JOSEPH A. POTENZA,* RAPHAEL M. ORNAF, KAREN E. RODRIQUES AND SPENCER KNAPP*

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, *USA*

AND ROGER A. LALANCETTE

Department of Chemistry, Rutgers, The State University of New Jersey, Newark, New Jersey 07102, *USA*

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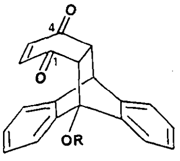
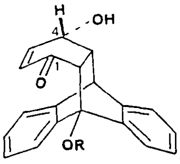
Abstract. $C_{28}H_{22}O_4$, $M_r = 422\cdot48$, orthorhombic, $P2_12_12_1$, $a = 13\cdot898\,(1)$, $b = 7\cdot285\,(1)$, $c = 20\cdot704\,(2)$ Å, $V = 2096\cdot2\,(6)$ Å^3, $Z = 4$, $D_m = 1\cdot32\,(1)$, $D_x = 1\cdot339$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu = 0\cdot54$ mm^{-1}, $F(000) = 888$, $T = 298\,(1)$ K, $R = 0\cdot052$ for 1285 observed reflections. The structure contains discrete molecules in which the 2-ene-1,4-dione rings are shallow boats with both carbonyl groups pointed away from an underlying benzene ring. One carbonyl O atom and the (benzyloxy)methoxy O atom are in close contact [2·810 (6) Å]. Several distances and angles in the vicinity of this contact show substantial deviations from expected values, indicating that the molecule is strained.

Introduction. As part of our work on aminocyclitol synthesis (Knapp, Ornaf & Rodriques, 1983), we became interested in site-selective reduction reactions of the 2-ene-1,4-dione (1). Specifically, reaction conditions were sought under which the C(4) carbonyl group could be reduced without reaction at C(1) as in (1)→(2) below. Although reagents can approach (1) from the *exo* face of the enedione ring without any apparent steric hindrance, borohydride reduction of (1) gave (2) in 99% yield without detectable reduction at C(1), implying that the (benzyloxy)methoxy group of (1) somehow slows reaction at C(1) relative to C(4) even though this group is behind the C(1) carbonyl. To help understand this difference in reactivity, the present structural analysis was undertaken.



(1), R CH$_2$OCH$_2$Ph



(2)

Experimental. Title compound prepared by Diels–Alder reaction of 9-[(benzyloxy)methoxy]anthracene with *p*-benzoquinone (Knapp *et al.*, 1983). Suitable crystals

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* To whom correspondence should be addressed.

from acetonitrile solution of the racemate. D_m by flotation in cyclohexanone/tetrabromoethane; colorless prism 0·33 × 0·20 × 0·15 mm; Syntex $P2_1$ diffractometer; graphite-monochromated Cu $K\alpha$ radiation; θ–2θ scan. Systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) consistent with $P2_12_12_1$. Cell constants from setting angles of 15 moderately intense reflections with $20{\cdot}57 \le \theta \le 41{\cdot}73°$; data corrected for decay, Lorentz, polarization, and absorption (numerical, $1{\cdot}16 < A < 1{\cdot}28$) effects. Variation in intensity of 3 standard reflections ±2%; 1575 unique reflections measured with $5 \le 2\theta \le 110°$; 1285 with $I \ge 2\sigma(I)$ used in refinement. Range of h,k,l: 0 to 14, 0 to 7, 0 to 21. With $Z = 4$, observed and calculated densities agreed well, fixing the asymmetric unit as one molecule. Therefore, since $P2_12_12_1$ contains no symmetry elements involving reflection/inversion, individual crystals of (1) are chiral. The absolute configuration of the crystal used was not determined.

Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); E map based on 300 phases revealed all 32 non-H atoms. H atoms at calculated positions with C—H distance = 0·95 Å. Temperature factors for H atoms set as $B_{\rm H} = B_N + 1$ before final cycles of refinement, where B_N is the temperature factor of the atom bonded to H; H-atom parameters not refined. Full-matrix least-squares refinement on F; all O atoms and all non-aromatic C atoms [C(1)–C(4), C(4a), C(9), C(9a), C(10), C(17), C(18)] anisotropic; aromatic C atoms refined isotropically to maintain data: parameter ratio >6. Secondary extinction parameter [final $g = 5{\cdot}7\,(9) \times 10^{-3}$] also refined; weights based on counting statistics. Final $R = 0{\cdot}052$, $wR = 0{\cdot}056$, $S = 2{\cdot}1$, $\Delta_{\max}/\sigma < 0{\cdot}1$. $\Delta\rho_{\max}$ 0·74, $\Delta\rho_{\min}$ −0·53 e Å^{-3}. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); programs used have been described previously (Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983). Final positional parameters and their e.s.d.'s are given in Table 1.*

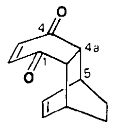
Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

	x	y	z	B or $B_{\rm eq}$* (Å^2)
O(1)	0·9300 (4)	0·8913 (7)	0·1179 (3)	7·5 (1)†
O(4)	1·2681 (3)	1·0596 (6)	0·0171 (2)	6·3 (1)†
O(9)	0·9784 (2)	0·5169 (5)	0·1162 (2)	3·9 (1)†
O(17)	0·9251 (3)	0·3579 (7)	0·2062 (2)	5·7 (1)†
C(1)	1·0077 (5)	0·9033 (9)	0·0903 (3)	4·6 (2)†
C(2)	1·0181 (4)	1·0292 (9)	0·0366 (3)	5·0 (2)†
C(3)	1·1026 (5)	1·0752 (9)	0·0117 (3)	5·1 (2)†
C(4)	1·1920 (4)	0·9992 (8)	0·0364 (3)	4·1 (2)†
C(4a)	1·1920 (4)	0·8432 (7)	0·0840 (2)	3·2 (1)†
C(5)	1·3281 (4)	0·4372 (8)	0·1215 (3)	3·8 (1)
C(6)	1·3223 (4)	0·3026 (9)	0·1685 (3)	4·4 (1)
C(7)	1·2348 (4)	0·2493 (9)	0·1932 (3)	4·5 (1)
C(8)	1·1495 (4)	0·3316 (9)	0·1716 (2)	3·9 (1)
C(8a)	1·1553 (3)	0·4702 (8)	0·1257 (2)	3·1 (1)
C(9)	1·0709 (3)	0·5776 (7)	0·0971 (2)	3·2 (1)†
C(9a)	1·0914 (3)	0·7895 (8)	0·1130 (2)	3·4 (1)†
C(10)	1·2372 (3)	0·6717 (8)	0·0500 (3)	3·5 (1)†
C(10a)	1·2440 (3)	0·5226 (7)	0·0999 (2)	3·2 (1)
C(11)	1·1669 (4)	0·6081 (7)	−0·0010 (3)	3·3 (1)
C(12)	1·0775 (3)	0·5613 (7)	0·0243 (2)	2·9 (1)
C(13)	1·0027 (4)	0·5119 (8)	−0·0164 (3)	4·2 (1)
C(14)	1·0206 (4)	0·4996 (9)	−0·0818 (3)	4·7 (1)
C(15)	1·1093 (4)	0·5386 (9)	−0·1066 (3)	5·0 (1)
C(16)	1·1840 (4)	0·5966 (9)	−0·0667 (3)	4·2 (1)
C(17)	0·9464 (4)	0·5313 (9)	0·1816 (3)	4·5 (2)†
C(18)	0·8489 (5)	0·2656 (9)	0·1716 (3)	5·8 (2)†
C(19)	0·7501 (4)	0·3277 (8)	0·1918 (3)	3·7 (1)
C(20)	0·6983 (4)	0·4506 (9)	0·1555 (3)	5·3 (1)
C(21)	0·6056 (5)	0·5038 (10)	0·1756 (3)	6·0 (2)
C(22)	0·5676 (4)	0·4352 (9)	0·2306 (3)	5·0 (1)
C(23)	0·6183 (4)	0·3133 (9)	0·2668 (3)	4·4 (1)
C(24)	0·7097 (4)	0·2578 (8)	0·2473 (3)	3·9 (1)

* $B_{\rm eq} = \frac{4}{3}(\beta_{11}a^2 + 2\beta_{12}ab\cos\gamma + \cdots)$.

† Atom refined anisotropically.

Discussion. A view of the title compound, showing the atom-numbering scheme, is given in Fig. 1 while bond lengths and angles are listed in Table 2. The enedione ring is a shallow boat: C(2), C(3), C(9a) and C(4a) are planar to within ±0·001 Å, and the two carbonyl groups are situated above this plane away from the underlying benzene ring, C(11)–C(16). Carbonyl atoms C(1) and C(4) show respective deviations from this plane of 0·126 and 0·104 Å, while the attached atoms O(1) and O(4) show respective deviations of 0·352 and 0·243 Å. The carbon deviations are slightly larger than those reported (0·07, 0·10 Å) for the comparison structure (3) (Greenhough & Trotter, 1980) which also contains a puckered 2-ene-1,4-dione ring. Clearly, in (1), the carbonyl containing C(1) is bent away from the underlying benzene ring to a greater extent than that containing C(4). This is also reflected in the dihedral angle each carbonyl makes with the conjugated C=C bond C(2)—C(3): 167·5° for O(1)—C(1)—C(2)—C(3), and 172·0° for O(4)—C(4)—C(3)—C(2).



(3)

Of particular relevance to the chemical-reactivity studies is the fact that O(1) and O(9) are in close non-bonded contact with the measured interatomic distance [2·810 (6) Å] virtually equal to the van der Waals diameter for oxygen (2·8 Å; Pauling, 1960). In addition, the C(9)—C(9a) bond [1·604 (7) Å] is significantly longer than the corresponding C(4a)—C(10) bond [1·565 (7) Å] on the other side of the molecule from the (benzyloxy)methoxy group. This latter distance compares well with the values of 1·552 (4) and 1·560 (3) Å reported for the corresponding bonds in

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* Lists of structure factors, H-atom coordinates, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42303 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(3), suggesting that the C(9)–C(9a) bond is lengthened because of steric strain related to the close O(1)···O(9) contact.

In the crystal, the (benzyloxy)methoxy group of (1) extends away from the bicyclo[2.2.2]octane unit. As indicated by the exocyclic bond angles with C(9) as vertex, O(9) is bent away from C(9a) and C(8a) [C(9a)–C(9)–O(9), 113·8 (4); C(8a)–C(9)–O(9), 115·3 (4)°] towards C(12) [C(12)–C(9)–O(9), 107·9 (4)°]. Atom C(17) is close to O(1), C(9a) and C(8a), as indicated by the non-bonded distances of 2·943 (9), 3·101 (8) and 3·156 (7) Å, respectively. While the position of O(9) is fixed to a large extent by the rigidity of the bicyclic system, there appears to be no obvious steric or electronic reason that would force C(17) to retain the same position in solution. The C(9)–O(9)–C(17) ether angle [121·6 (4)°] is 8·2 (6)° larger than the presumably unstrained C(17)–O(17)–C(18) angle [113·4 (5)°] located further down the chain. Finally, the O(1)–C(1)···C(9)–O(9) dihedral angle is 13·1° and the sense is such that, looking down the C(1)···C(9) direction with the C(1)→O(1) vector horizontal as in (4), O(9) lies below O(1). This sense is opposite from that which might be expected from a casual examination of a line drawing of the molecule, such as (1).

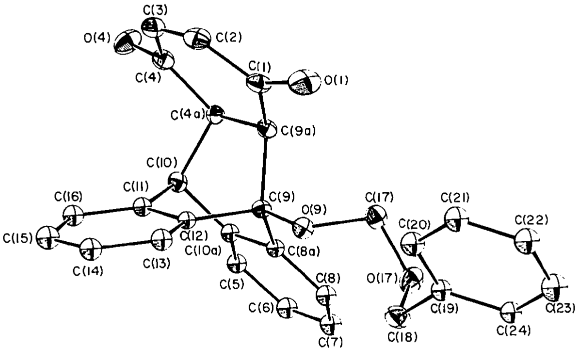
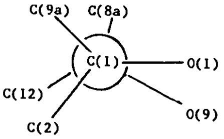


Fig. 1. View of the title compound showing the atom-numbering scheme. H atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 15% probability level.

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)–C(1)	1·226 (6)	C(8a)–C(10a)	1·397 (6)
O(4)–C(4)	1·213 (6)	C(9)–C(9a)	1·604 (7)
O(9)–C(9)	1·417 (5)	C(9)–C(12)	1·545 (7)
O(9)–C(17)	1·428 (6)	C(10)–C(10a)	1·503 (7)
O(17)–C(17)	1·394 (8)	C(10)–C(11)	1·512 (6)
O(17)–C(18)	1·445 (7)	C(11)–C(12)	1·391 (6)
C(1)–C(9a)	1·503 (7)	C(11)–C(16)	1·383 (7)
C(1)–C(2)	1·449 (9)	C(12)–C(13)	1·386 (6)
C(2)–C(3)	1·327 (8)	C(13)–C(14)	1·379 (7)
C(3)–C(4)	1·454 (8)	C(14)–C(15)	1·365 (7)
C(4)–C(4a)	1·504 (7)	C(15)–C(16)	1·392 (7)
C(4a)–C(9a)	1·571 (6)	C(18)–C(19)	1·505 (7)
C(4a)–C(10)	1·565 (7)	C(19)–C(20)	1·374 (8)
C(5)–C(6)	1·384 (8)	C(19)–C(24)	1·376 (7)
C(5)–C(10a)	1·397 (6)	C(20)–C(21)	1·406 (8)
C(6)–C(7)	1·374 (7)	C(21)–C(22)	1·350 (8)
C(7)–C(8)	1·401 (7)	C(22)–C(23)	1·359 (8)
C(8)–C(8a)	1·389 (7)	C(23)–C(24)	1·393 (7)
C(8a)–C(9)	1·529 (6)		

C(9)–O(9)–C(17)	121·6 (4)	C(4a)–C(9a)–C(9)	108·6 (4)
C(17)–O(17)–C(18)	113·4 (5)	C(4a)–C(10)–C(10a)	107·0 (4)
C(2)–C(1)–O(1)	119·4 (6)	C(4a)–C(10)–C(11)	107·5 (4)
C(2)–C(1)–C(9a)	120·8 (5)	C(10a)–C(10)–C(11)	107·4 (4)
O(1)–C(1)–C(9a)	119·8 (6)	C(5)–C(10a)–C(8a)	119·6 (5)
C(1)–C(2)–C(3)	123·1 (5)	C(5)–C(10a)–C(10)	126·4 (4)
C(2)–C(3)–C(4)	121·6 (6)	C(8a)–C(10a)–C(10)	113·9 (4)
C(3)–C(4)–O(4)	119·4 (6)	C(10)–C(11)–C(12)	112·9 (4)
C(3)–C(4)–C(4a)	121·2 (5)	C(10)–C(11)–C(16)	126·5 (4)
C(4a)–C(4)–O(4)	119·4 (5)	C(12)–C(11)–C(16)	120·6 (5)
C(4)–C(4a)–C(9a)	116·0 (3)	C(9)–C(12)–C(11)	114·1 (4)
C(4)–C(4a)–C(10)	107·9 (4)	C(9)–C(12)–C(13)	125·5 (4)
C(9a)–C(4a)–C(10)	109·2 (4)	C(11)–C(12)–C(13)	120·3 (5)
C(6)–C(5)–C(10a)	119·4 (4)	C(12)–C(13)–C(14)	118·6 (5)
C(5)–C(6)–C(7)	120·9 (5)	C(13)–C(14)–C(15)	121·2 (5)
C(6)–C(7)–C(8)	120·6 (5)	C(14)–C(15)–C(16)	120·9 (5)
C(7)–C(8)–C(8a)	118·7 (4)	C(11)–C(16)–C(15)	118·3 (5)
C(8)–C(8a)–C(9)	126·4 (4)	O(9)–C(17)–O(17)	110·2 (5)
C(8)–C(8a)–C(10a)	120·7 (4)	O(17)–C(18)–C(19)	113·0 (5)
C(9)–C(8a)–C(10a)	112·9 (4)	C(18)–C(19)–C(20)	121·4 (5)
C(8a)–C(9)–C(9a)	106·1 (4)	C(18)–C(19)–C(24)	119·6 (5)
C(8a)–C(9)–C(12)	107·5 (4)	C(24)–C(19)–C(20)	119·0 (5)
C(8a)–C(9)–O(9)	115·3 (4)	C(19)–C(20)–C(21)	119·7 (6)
C(9a)–C(9)–C(12)	105·6 (4)	C(20)–C(21)–C(22)	120·4 (6)
C(9a)–C(9)–O(9)	113·8 (4)	C(21)–C(22)–C(23)	120·2 (6)
C(12)–C(9)–O(9)	107·9 (4)	C(22)–C(23)–C(24)	120·2 (6)
C(1)–C(9a)–C(4a)	115·6 (4)	C(19)–C(24)–C(23)	120·4 (5)
C(1)–C(9a)–C(9)	109·3 (4)		



(4)

Taken together, these structural data show that there is substantial crowding and strain in the region *endo* to the C(1) carbonyl, and this may be related to its relative inertness to reduction. To help resolve the nature of this site-selective reduction further, and to determine the extent to which it arises from electronic factors, molecular-orbital calculations of (1) are being performed and the reactivity of the all-carbon analogue of (1) [*e.g.* (1) with O(9) and O(17) replaced by CH_2 groups] is being studied.

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