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Structure of Benz[*a*]anthracene-7,12-dione

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Abstract. C₁₈H₁₀O₂, monoclinic, C2/c, $a = 10.918$ (1), $b = 11.369$ (1), $c = 19.850$ (1) Å, $\beta = 97.224$ (7)°, $U = 2444.4$ Å³, $Z = 8$, $D_m = 1.41$ (2), $D_c = 1.403$ Mg m⁻³, $F(000) = 1072$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.742$ mm⁻¹. 2253 reflections were measured, of which 1039 had significant intensities. Refinement converged to a final R of 0.045. The molecule is approximately planar. Ring C is significantly non-delocalized. Bonds C(3)-C(4) and C(5)-C(6) are short, and indicate pronounced olefinic character for these bonds.

Introduction. The polycyclic aromatic hydrocarbon benz[*a*]anthracene is a well established weak carcinogen (Searle, 1976). Its biological activity results from metabolic activation to reactive species, such as the 9,10-diol 11,12-epoxide or the 5,6-epoxide (Harvey, 1981). Particular regions of reactivity of the benz[*a*]anthracene molecule, such as 'K' and 'bay' regions, are therefore especially susceptible to electrophilic attack. This is seen, for example, by the olefinic character of the K region in various methyl-substituted benz[*a*]anthracene structures.

In this study, we describe the structure of a non-carcinogenic derivative of benz[*a*]anthracene, and compare its geometry with that of various other benz[*a*]anthracene derivatives, all of which show at least some carcinogenic activity. The structure described in this paper is that of the 7,12-dione derivative (BA dione), which appears to have little or no tumorigenic activity following injection into mice (*Survey of Compounds which have been Tested for Carcinogenic Activity*, 1971-1972).

Experimental. Prismatic crystals of BA dione were grown from alcoholic solution, which showed monoclinic symmetry when examined by oscillation and Weissenberg photography. Accurate cell dimensions were obtained by measurement of 25 θ values on an Enraf-Nonius CAD-4 diffractometer. Intensity data were collected on the diffractometer using graphite-monochromated Cu $K\alpha$ radiation and an ω -2 θ scan technique ($1.5 < \theta < 65.0^\circ$). Only 1039 of the 2253 unique reflections measured had significant intensity [$I > 2.0\sigma(I)$]. No crystal decomposition was recorded during data collection.

The structure was routinely solved by direct methods and refined by full-matrix least-squares techniques to a final R of 0.045 and a weighted R_w of 0.049. Weights used were of the form $1/[\sigma^2(F_o^2) + (0.03F_o^2)^2]^{1/2}$. H-atom positions were located in a difference Fourier synthesis; these, together with individual H-atom isotropic thermal parameters, were included in the refinement. All calculations were performed on a PDP 11/34A computer using the Enraf-Nonius SDP program system, together with others written by S. Islam. Coordinates and thermal parameters are given in Table 1.*

* Lists of structure factors and anisotropic thermal parameters, together with Table 4, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36670 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$ for C and O, $\times 10^3$ for H atoms) and isotropic thermal parameters with *e.s.d.*'s in parentheses

For non-H atoms, $B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B (\AA^2)
C(1)	7776 (3)	1829 (3)	6842 (2)	5.67 (2)
C(2)	8029 (3)	2385 (3)	7459 (2)	6.87 (2)
C(3)	7440 (4)	3437 (3)	7605 (2)	7.47 (2)
C(4)	6641 (3)	3934 (3)	7129 (2)	7.03 (2)
C(4 <i>a</i>)	6354 (3)	3414 (3)	6469 (2)	5.53 (2)
C(5)	5549 (3)	3990 (3)	5970 (2)	6.23 (2)
C(6)	5289 (3)	3522 (3)	5344 (2)	5.70 (2)
C(6 <i>a</i>)	5791 (3)	2424 (3)	5184 (1)	4.50 (1)
C(7)	5422 (3)	1963 (3)	4491 (2)	5.23 (2)
C(7 <i>a</i>)	5879 (2)	804 (3)	4309 (1)	4.47 (1)
C(8)	5553 (3)	355 (3)	3658 (2)	5.90 (2)
C(9)	5974 (3)	-744 (3)	3502 (2)	6.43 (2)
C(10)	6710 (3)	-1385 (3)	3979 (2)	6.23 (2)
C(11)	7031 (3)	-942 (3)	4621 (2)	5.23 (1)
C(11 <i>a</i>)	6621 (2)	153 (3)	4787 (1)	4.10 (1)
C(12)	7001 (3)	626 (3)	5492 (1)	4.57 (1)
C(12 <i>a</i>)	6573 (3)	1815 (3)	5667 (1)	4.37 (1)
C(12 <i>b</i>)	6919 (3)	2327 (3)	6333 (1)	4.57 (1)
O(7)	4742 (2)	2545 (2)	4078 (1)	7.50 (1)
O(12)	7633 (2)	-5 (2)	5888 (1)	6.90 (1)
H(1)	821 (2)	99 (2)	674 (1)	5.7 (7)
H(2)	862 (3)	199 (3)	782 (2)	9.8 (10)
H(3)	774 (3)	382 (3)	808 (2)	9.7 (10)
H(4)	613 (2)	470 (2)	722 (1)	6.3 (7)
H(5)	513 (3)	472 (3)	616 (1)	9.4 (7)
H(6)	471 (3)	387 (3)	497 (1)	8.1 (8)
H(8)	498 (3)	83 (3)	323 (1)	7.9 (8)
H(9)	576 (2)	-106 (2)	306 (1)	6.1 (7)
H(10)	698 (3)	-214 (3)	385 (1)	8.3 (9)
H(11)	760 (2)	-136 (2)	501 (1)	6.4 (7)

Discussion. The molecular structure of BA dione is shown in Fig. 1. Tables 2 and 3 detail the molecular geometry of the molecule, with the former comparing bond distances with those in other benz[*a*]anthracene structures.

The carbonyl groups at positions 7 and 12 have produced alterations in the geometry of the ring to which they are attached, compared to other benz[*a*]anthracene structures (Table 2). Thus, bonds C(11*a*)–C(12), C(12)–C(12*a*), C(7)–C(7*a*) and C(6*a*)–C(7) in BA dione are significantly longer than

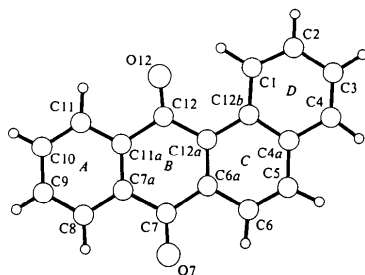


Fig. 1. The molecular structure of BA 7,12-dione.

in the other structures; their average bond length of 1.485 Å in the dione is virtually that expected for a C(sp^2)–C(sp^2) single bond. In addition, bonds C(7*a*)–C(11*a*) and C(6*a*)–C(12*a*) in BA dione are significantly shorter than in the other benz[*a*]anthracene structures. The overall pattern of bond geometry in the present structure suggests that ring C is less delocalized and aromatic than in other benz[*a*]anthracene structures. The abnormal shortness of bond C(3)–C(4) may be related to this feature. Bond C(5)–C(6), the *K*-region bond, displays its expected shortening compared to a pure aromatic bond, and thus it would be expected that this bond in BA dione would be susceptible to metabolic activation to, for example, a 5,6-epoxide.

Table 4* (deviations of atoms from least-squares planes) and Fig. 2 show that the BA dione molecule is approximately planar, with each six-membered ring being coplanar within experimental error. The maximum twisting in the molecule is between rings A and D, which are at an angle of 7° to each other. The close 2.058 Å interaction between O(12) and H(1), the proton on C(1), has resulted in the C(1)–C(12*b*)–C(12*a*)–C(12) torsion angle being 7.3 (5)°, and possibly in the distortions from planarity. This interaction has also resulted in O(12) being pushed away from H(1), as shown by the asymmetry in the exocyclic bond angles around C(12). No structural data on benz[*a*]anthracene itself are available, although (\pm)-8 α ,9 β ,10 β ,11 α -tetrahydroxy-8,9,10,11-tetrahydrobenz[*a*]anthracene (Neidle, Cooper & Ribeiro, 1981) has an approximately planar tricyclic ABC ring system. Other methyl-substituted benz[*a*]anthracenes (Table 2) are invariably non-planar; they have methyl groups either at the 12 or 1 position, thereby producing close contacts involving bay-region protons.

* See deposition footnote.

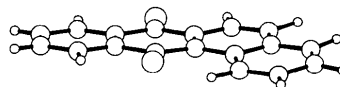


Fig. 2. A view of the structure along the molecular plane.

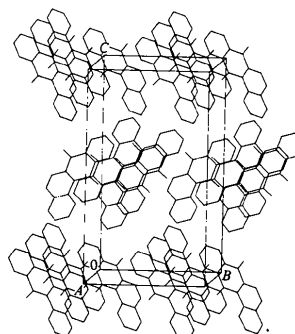


Fig. 3. A view of the unit-cell contents.

Table 2. Bond distances (Å) in BA dione, together with distances in other benz[a]anthracene structures

	BA dione	(a)	(b)	(c)	(d)	(e)	(f)
C(1)—C(2)	1.377 (4)	1.348 (11)	1.41	1.39	1.372 (8)	1.384	1.378
C(1)—C(12b)	1.406 (4)	1.443 (8)	1.44	1.41	1.420 (7)	1.401	1.409
C(2)—C(3)	1.405 (5)	1.370 (11)	1.36	1.38	1.402 (9)	1.409	1.380
C(3)—C(4)	1.328 (5)	1.380 (9)	1.35	1.37	1.388 (10)	1.359	1.381
C(4)—C(4a)	1.436 (4)	1.393 (12)	1.42	1.42	1.410 (10)	1.423	1.390
C(4a)—C(5)	1.401 (4)	1.429 (9)	1.44	1.43	1.465 (9)	1.420	1.471
C(4a)—C(12b)	1.423 (4)	1.386 (11)	1.41	1.41	1.434 (8)	1.421	1.416
C(5)—C(6)	1.348 (4)	1.349 (12)	1.34	1.34	1.326 (10)	1.335	1.460
C(6)—C(6a)	1.415 (4)	1.434 (11)	1.45	1.44	1.427 (9)	1.446	1.487
C(6a)—C(7)	1.480 (4)	1.373 (12)	1.37	1.39	1.372 (9)	1.391	1.374
C(6a)—C(12a)	1.386 (3)	1.428 (8)	1.43	1.44	1.455 (8)	1.447	1.450
C(7)—C(7a)	1.470 (4)	1.375 (10)	1.40	1.41	1.411 (9)	1.406	1.426
C(7)—O(7)	1.228 (3)	—	—	—	—	—	—
C(7a)—C(8)	1.393 (4)	1.496 (11)	1.44	1.43	1.375 (9)	1.445	1.412
C(7a)—C(11a)	1.383 (3)	1.418 (8)	1.42	1.43	1.450 (8)	1.429	1.417
C(8)—C(9)	1.380 (5)	1.523 (10)	1.36	1.36	1.365 (10)	1.351	1.367
C(9)—C(10)	1.373 (4)	1.537 (7)	1.39	1.42	1.457 (10)	1.411	1.399
C(10)—C(11)	1.374 (4)	1.492 (11)	1.37	1.37	1.400 (9)	1.368	1.365
C(11)—C(11a)	1.378 (4)	1.503 (10)	1.42	1.42	1.438 (8)	1.425	1.424
C(11a)—C(12)	1.506 (3)	1.383 (11)	1.41	1.43	1.412 (8)	1.429	1.431
C(12)—O(12)	1.214 (3)	—	—	—	—	—	—
C(12)—C(12a)	1.485 (4)	1.412 (10)	1.39	1.39	1.373 (8)	1.396	1.385
C(12a)—C(12b)	1.451 (4)	1.443 (11)	1.47	1.48	1.498 (8)	1.481	1.492

(a) (\pm)-8 α ,9 β ,10 β ,11 α -Tetrahydroxy-8,9,10,11-tetrahydrobenz[a]anthracene (Neidle, Cooper & Ribeiro, 1981). (b) 1-Methylbenz[a]anthracene (Jones & Sowden, 1979). Average e.s.d. is 0.01 Å. (c) 12-Methylbenz[a]anthracene (Jones & Sowden, 1976). Average e.s.d. is 0.012 Å. (d) 1,12-Dimethylbenz[a]anthracene (Jones, Sowden, Hazell & Hazell, 1978). Weighted mean values and e.s.d.'s from two independent determinations are given. (e) 7,12-Dimethylbenz[a]anthracene (Iball, 1964). Average e.s.d.'s are stated to be less than 0.01 Å. (f) 7,12-Dimethylbenz[a]anthracene 5,6-oxide (Glusker, Carrell & Zacharias, 1974). E.s.d.'s are 0.003–0.004 Å.

Table 3. Bond angles (°) in BA dione, for the non-H atoms

C(2)—C(1)—C(12b)	119.7 (4)	C(8)—C(7a)—C(11a)	120.1 (3)
C(1)—C(2)—C(3)	121.9 (4)	C(7a)—C(8)—C(9)	119.0 (4)
C(2)—C(3)—C(4)	119.5 (4)	C(8)—C(9)—C(10)	120.6 (4)
C(3)—C(4)—C(4a)	121.5 (4)	C(9)—C(10)—C(11)	120.3 (4)
C(4)—C(4a)—C(5)	119.9 (4)	C(10)—C(11)—C(11a)	120.0 (3)
C(4)—C(4a)—C(12b)	118.8 (3)	C(7a)—C(11a)—C(11)	120.0 (3)
C(5)—C(4a)—C(12b)	121.3 (3)	C(7a)—C(11a)—C(12)	121.0 (3)
C(4a)—C(5)—C(6)	120.5 (4)	C(11)—C(11a)—C(12)	119.0 (3)
C(5)—C(6)—C(6a)	120.9 (4)	C(11a)—C(12)—C(12a)	118.9 (3)
C(6)—C(6a)—C(7)	117.0 (3)	C(11a)—C(12)—O(12)	117.3 (3)
C(6)—C(6a)—C(12a)	120.5 (3)	C(12a)—C(12)—O(12)	123.8 (3)
C(7)—C(6a)—C(12a)	122.6 (3)	C(6a)—C(12a)—C(12)	118.5 (3)
C(6a)—C(7)—C(7a)	119.0 (3)	C(6a)—C(12a)—C(12b)	119.8 (3)
C(6a)—C(7)—O(7)	120.1 (3)	C(12)—C(12a)—C(12b)	121.7 (3)
C(7a)—C(7)—O(7)	120.9 (3)	C(1)—C(12b)—C(4a)	118.6 (3)
C(7)—C(7a)—C(8)	120.1 (3)	C(1)—C(12b)—C(12a)	124.5 (3)
C(7)—C(7a)—C(11a)	119.9 (3)	C(4a)—C(12b)—C(12a)	117.9 (3)

The crystal structure involves BA 7,12-dione molecules associating together by weak van der Waals forces (see Fig. 3). There are no hydrogen bonds in the structure.

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