

cis-3,4,4a,9,10,10a-Hexahydro-1,4a-ethanophenanthrene-2(1H),12-dione, C₁₆H₁₆O₂

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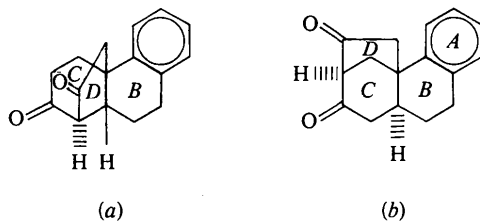
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Abstract. $M_r = 240.3$, m.p. = 417 K, orthorhombic, $Pca2_1$, $a = 11.385$ (9), $b = 11.938$ (8), $c = 18.50$ (2) Å, $V = 2514.4$ Å³, $Z = 8$, $D_x = 1.270$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 5.22$ cm⁻¹, $F(000) = 1024$, room temperature. $R = 0.044$ for 1472 reflections with $|F_o| > 2\sigma(|F_o|)$. Of the three six-membered and one five-membered rings in the molecule, the phenyl ring is substantially planar, the other two six-membered rings are in half-boat and distorted chair conformations, while the five-membered ring is intermediate between envelope and half-chair. The two non-aromatic six-membered rings are *cis* fused. The asymmetric unit contains two crystallographically independent molecules of similar geometry. The structure shows considerable strain; formally tetrahedral C–C–C bond angles vary from 100.9 (3) to 116.6 (4)°, the greatest distortion being in the five-membered ring.

Introduction. Synthesis of isomeric bridged diketones (a) and (b) from epimeric *cis* and *trans* acetal aldehydes by mild-acid-catalysed deacetylation and intramolecular aldol condensation followed by oxidation of the intermediate bridged ketols was reported by Sinha *et al.* (1983). X-ray analyses of these compounds were undertaken as part of our programme to study the relative influence of the ring-junction stereochemistry of these derivatives on the regioselectivity in such cyclizations. The present paper describes the crystal and molecular structure of the *cis*-bridged diketone (a); that of the *trans* compound (b) is reported in the following paper (Mukherjee & Mukherjee, 1984).



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Experimental. Crystals kindly supplied by Professor U. R. Ghatak, IACS, Calcutta; oscillation and Weissenberg photographs indicated orthorhombic symmetry, confirmed by diffractometric analysis; cell parameters from the 2θ values of 25 randomly chosen reflections, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated $Cu K\alpha$ radiation; crystal $0.25 \times 0.22 \times 0.18$ mm, $5 \leq \theta \leq 55^\circ$, ω - 2θ scan; 1661 reflections measured, 1472 with $|F_o| > 2\sigma(|F_o|)$; index range h 0–12, k 0–12, l 0–19, no crystal decomposition during data collection; no correction for absorption; systematic absences indicated $Pbcm$ or $Pca2_1$; distribution of normalized structure amplitudes $|E|$ favoured $Pca2_1$, with the asymmetric unit containing two molecules; structure solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); 12 non-hydrogen atoms of one molecule located from E map. Fourier synthesis completed three six-membered rings of one molecule but without any success in finding the second molecule in the asymmetric unit. In a subsequent *MULTAN* run the known orientation of the fragment of one molecule with random position was used as input. The E map computed from the best phase set characterized by a combined FOM 2.60 revealed all 36 non-hydrogen atoms; positions of hydrogen atoms determined by standard geometry; final refinement by block-diagonal least squares, anisotropic for non-hydrogen atoms, positions and isotropic temperature factors of H atoms fixed, $R = 0.044$, $wR = 0.051$ for 1472 reflections; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma^2(F)$; for $|F_o| \leq 5.0$, $\sigma(F) = 0.42|F_o|$; for $5.0 < |F_o| \leq 6.5$, $\sigma(F) = 0.28|F_o|$; for $6.5 < |F_o| \leq 7.9$, $\sigma(F) = 0.22|F_o|$; for $7.9 < |F_o| \leq 14.8$, $\sigma(F) = 0.17|F_o|$; for $14.8 < |F_o| \leq 27.9$, $\sigma(F) = 0.11|F_o|$; for $|F_o| > 27.9$, $\sigma(F) = 0.05|F_o|$ (Seal & Ray, 1981); in final cycle of refinement, max. $\Delta/\sigma = 0.703$, max. positive and negative peak heights in final difference Fourier +0.3 and $-0.2 e \text{ \AA}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all computations performed on the Burroughs B6700 computer at the Regional Computer Centre, Jadavpur University Campus, Calcutta; *MULTAN78* (Main *et*

al., 1978) and XRAY ARC (Vickery, Bright & Mallinson, 1971).

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) of the non-hydrogen atoms with e.s.d.'s

Molecule 1	x	y	z	$B_{eq} = \frac{1}{3} \sum B_{ii}$
C(1)	-926 (3)	4394 (4)	1049 (2)	4.0 (2)
C(2)	-1540 (4)	4523 (4)	404 (3)	4.6 (2)
C(3)	-2394 (4)	3803 (4)	202 (3)	5.4 (3)
C(4)	-2691 (4)	2899 (4)	639 (3)	5.2 (3)
C(5)	-2085 (4)	2736 (4)	1286 (3)	4.4 (2)
C(6)	-1203 (3)	3480 (3)	1493 (2)	3.5 (2)
C(7)	-545 (3)	3343 (3)	2202 (2)	3.2 (2)
C(8)	-1133 (4)	4054 (4)	2793 (3)	4.1 (2)
C(9)	-428 (5)	4081 (4)	3497 (3)	4.9 (3)
C(10)	871 (4)	4114 (3)	3384 (3)	4.3 (2)
C(11)	1309 (3)	3359 (4)	2793 (2)	3.9 (2)
C(12)	729 (3)	3739 (3)	2082 (2)	3.3 (2)
C(13)	882 (4)	4961 (4)	1873 (3)	4.3 (2)
C(14)	24 (6)	5222 (5)	1225 (3)	6.0 (3)
C(15)	768 (4)	2207 (3)	2898 (2)	4.3 (2)
C(16)	-358 (4)	2145 (3)	2471 (2)	3.7 (2)
O(1)	1178 (3)	1470 (3)	3272	5.6 (2)
O(2)	1538 (3)	4703 (3)	3730 (2)	6.0 (2)

Molecule 2	x	y	z	B_{eq}
C(1)	3257 (4)	1346 (4)	5655 (3)	4.4 (2)
C(2)	2796 (4)	1024 (4)	6319 (3)	5.1 (3)
C(3)	3249 (5)	117 (5)	6683 (3)	5.8 (3)
C(4)	4187 (5)	-481 (4)	6419 (3)	5.4 (3)
C(5)	4657 (4)	-171 (4)	5746 (3)	4.7 (3)
C(6)	4215 (3)	741 (3)	5367 (2)	3.9 (2)
C(7)	4697 (3)	1062 (3)	4639 (2)	3.5 (2)
C(8)	4001 (4)	487 (3)	4045 (3)	4.1 (2)
C(9)	4311 (5)	868 (4)	3271 (3)	5.2 (3)
C(10)	4620 (4)	2085 (4)	3225 (3)	4.9 (2)
C(11)	5327 (4)	2535 (3)	3859 (3)	4.6 (2)
C(12)	4617 (4)	2344 (3)	4554 (2)	3.9 (2)
C(13)	3357 (4)	2748 (4)	4587 (3)	5.1 (2)
C(14)	2768 (4)	2356 (4)	5275 (3)	5.5 (3)
C(15)	6366 (4)	1740 (4)	3975 (3)	4.8 (2)
C(16)	6012 (3)	860 (4)	4523 (3)	4.5 (2)
O(1)	7301 (3)	1825 (3)	3683 (3)	7.0 (2)
O(2)	4350 (4)	2652 (3)	2707 (2)	7.2 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s

Molecule 1		Molecule 2	
C(1)-C(2)	1.392 (6)	C(8)-C(9)	1.530 (7)
C(1)-C(6)	1.401 (6)	C(9)-C(10)	1.494 (7)
C(1)-C(14)	1.501 (7)	C(10)-C(11)	1.503 (6)
C(2)-C(3)	1.350 (7)	C(11)-C(12)	1.540 (6)
C(3)-C(4)	1.390 (7)	C(11)-C(15)	1.519 (6)
C(4)-C(5)	1.396 (7)	C(12)-C(13)	1.513 (6)
C(5)-C(6)	1.395 (6)	C(13)-C(14)	1.535 (8)
C(6)-C(7)	1.519 (6)	C(15)-C(16)	1.508 (6)
C(7)-C(8)	1.539 (6)	C(15)-O(1)	1.213 (5)
C(7)-C(12)	1.542 (5)	C(10)-O(2)	1.220 (6)
C(7)-C(16)	1.529 (5)		

Molecule 1		Molecule 2	
C(2)-C(1)-C(6)	118.4 (4)	C(8)-C(9)-C(10)	113.6 (4)
C(2)-C(1)-C(14)	118.3 (4)	C(9)-C(10)-C(11)	114.5 (4)
C(6)-C(1)-C(14)	123.2 (4)	C(9)-C(10)-O(2)	124.0 (4)
C(1)-C(2)-C(3)	121.9 (4)	C(11)-C(10)-O(2)	121.5 (4)
C(2)-C(3)-C(4)	120.5 (5)	C(10)-C(11)-C(12)	107.6 (3)
C(3)-C(4)-C(5)	119.2 (5)	C(10)-C(11)-C(15)	108.3 (3)
C(4)-C(5)-C(6)	120.2 (4)	C(12)-C(11)-C(15)	101.7 (3)
C(1)-C(6)-C(5)	119.8 (4)	C(7)-C(12)-C(11)	100.9 (3)
C(1)-C(6)-C(7)	118.6 (4)	C(7)-C(12)-C(13)	113.5 (3)
C(5)-C(6)-C(7)	121.6 (4)	C(11)-C(12)-C(13)	118.2 (3)
C(6)-C(7)-C(8)	109.9 (3)	C(12)-C(13)-C(14)	110.7 (4)
C(6)-C(7)-C(12)	107.9 (3)	C(1)-C(14)-C(13)	117.6 (4)
C(6)-C(7)-C(16)	116.8 (3)	C(11)-C(15)-C(16)	108.8 (4)
C(8)-C(7)-C(12)	110.1 (3)	C(11)-C(15)-O(1)	125.1 (4)
C(8)-C(7)-C(16)	110.2 (3)	C(16)-C(15)-O(1)	126.2 (4)
C(12)-C(7)-C(16)	101.7 (3)	C(7)-C(16)-C(15)	104.1 (3)
C(7)-C(8)-C(9)	112.9 (4)		

Discussion. Final atomic parameters and interatomic distances and angles with e.s.d.'s are given in Tables 1* and 2. Perspective views of the asymmetric unit with the atom-numbering scheme and of the packing are shown in Figs. 1 and 2. Of the three six-membered (A, B, C) and one five-membered (D) rings in the molecule the phenyl ring A is planar and ring B assumes a half-boat conformation with C(12) lying outside the least-squares plane through C(1), C(6), C(7), C(13) and C(14) (Geise, Altona & Romers, 1967). The conformation of ring C, with torsion-angle summation $\sim 330^\circ$ and individual torsion angles ranging from $36.0 (7)^\circ$ to $70.5 (7)^\circ$, is a distorted chair while that of ring D is intermediate between envelope and half-chair.

* Lists of structure amplitudes, anisotropic thermal parameters, ring torsion angles and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39140 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

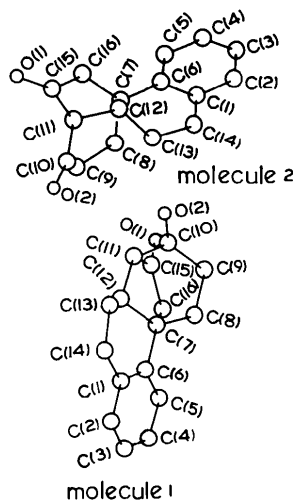


Fig. 1. Perspective view of the asymmetric unit along b.

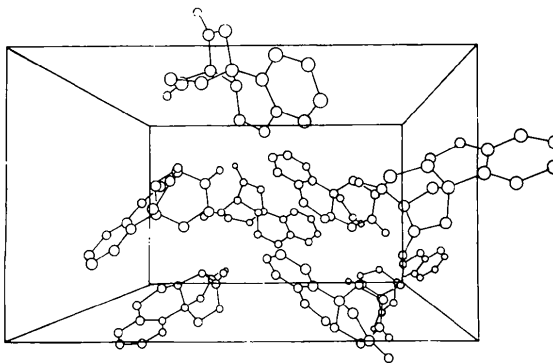


Fig. 2. Packing arrangement viewed along b.

Similar observations were reported in bridged cyclopentane systems (Fuchs, 1978) and steroid structures (Altona, Geise & Romers, 1968). The amount of distortion in each case can be discerned from the deviation of observed torsion angles from the computed values for appropriately substituted rings of these conformations (Bucourt & Hainaut, 1965). The distortions can be understood in terms of conformational transmission effects (Barton, 1970). As a result, some of the C—C—C valence angles, especially in ring *D*, deviate considerably from the tetrahedral value. Torsion angles of the same sign about C(7)—C(12) for rings *B* and *C* [C(6)—C(7)—C(12)—C(13) and C(8)—C(7)—C(12)—C(11)], +62.0 (7), +69.3 (7)° for molecule 1 and -61.3 (7), -68.8 (7)° for molecule 2, show that the *B/C* junction is *cis* (Bucourt, 1974). The dihedral angles 4.5 (7), 94.0 (6), 7.9 (6)° (molecule 1) and 3.1 (7), 95.2 (6), 71.4 (6)° (molecule 2) between ring *A* and the planar part of ring *B* and between the planar parts of rings *B*, *C* and *C*, *D* clearly indicate that the two crystallographically independent molecules in the asymmetric unit are of similar geometry. The angle between the phenyl rings of the two molecules is 82.5 (5)°. The crystal structure consists of discrete molecules with no intermolecular distance shorter than the sum of the van der Waals radii (Pauling, 1960).

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***trans*-3,4,4a,9,10,10a-Hexahydro-3,4a-ethanophenanthrene-2(1*H*),12-dione, C₁₆H₁₆O₂**

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Abstract. $M_r = 240.3$, m.p. = 435 K, monoclinic, $P2_1$, $a = 8.638$ (1), $b = 7.160$ (1), $c = 10.554$ (1) Å, $\beta = 104.08$ (1)°, $V = 633.2$ Å³, $Z = 2$, $D_x = 1.26$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.88$ cm⁻¹, $F(000) = 256$, room temperature, $R = 0.044$ for 1080 reflections with $|F_o| > 2\sigma(|F_o|)$. Of the three six-membered and one five-membered rings in the molecule the phenyl ring is

planar, the other two six-membered rings assume distorted half-chair and chair conformations while that of the five-membered ring is an envelope. The two non-aromatic six-membered rings are *trans* fused. The structure exhibits considerable strain, 'tetrahedral' C—C—C valence angles vary from 102.0 (4) to 115.1 (4)°, the five-membered ring being distorted most.