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).

The authors wish to thank Professor U. R. Ghatak, IACS, Calcutta, for supplying the title compound, Dr S. Ray, IACS, Calcutta, for stimulating discussions and Dr S. Roy, RCC, Calcutta, for constant encouragement and unfailing assistance during computation.

References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

BARTON, D. H. R. (1970). *Science*, **169**, 539–544.

BUCOURT, R. (1974). *Topics in Stereochemistry*, Vol. 8, edited by E. L. ELIEL & N. L. ALLINGER, pp. 159–224. New York: John Wiley.

BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

FUCHS, B. (1978). *Topics in Stereochemistry*, Vol. 10, edited by E. L. ELIEL & N. L. ALLINGER, pp. 1–94. New York: John Wiley.

GEISE, H. J., ALTONA, C. & ROMERS, C. (1967). *Tetrahedron*, **23**, 439–463.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MUKHERJEE, M. & MUKHERJEE, A. K. (1984). *Acta Cryst.* C**40**, 983–985.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

SEAL, A. & RAY, S. (1981). *Indian J. Phys.* **55**A, 414–416.

SINHA, G., MAJI, S. K., GHATAK, U. R., MUKHERJEE, M., MUKHERJEE, A. K. & CHAKRAVORTY, A. K. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 2519–2528.

VICKERY, B. L., BRIGHT, D. & MALLINSON, P. R. (1971). *XRAY ARC.* IBM 1130 program system for crystallography modified for the Burroughs B6700 computer.

Acta Cryst. (1984). C**40**, 983–985

trans-3,4,4a,9,10,10a-Hexahydro-3,4a-ethanophenanthrene-2(1*H*),12-dione, $C_{16}H_{16}O_2$

BY MONIKA MUKHERJEE (NÉE MONDAL)

Department of Magnetism, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, *India*

AND A. K. MUKHERJEE

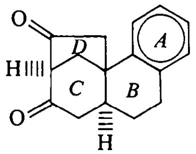
Department of Physics, Jadavpur University, Calcutta 700032, *India*

(*Received* 6 *July* 1983; *accepted* 19 *December* 1983)

Abstract. $M_r = 240{\cdot}3$, m.p. = 435 K, monoclinic, $P2_1$, $a = 8{\cdot}638$ (1), $b = 7{\cdot}160$ (1), $c = 10{\cdot}554$ (1) Å, $\beta = 104{\cdot}08$ (1)°, $V = 633{\cdot}2$ Å^3, $Z = 2$, $D_x = 1{\cdot}26$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}88$ cm^{-1}, $F(000) = 256$, room temperature, $R = 0{\cdot}044$ 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.

0108-2701/84/060983-03$01.50

Introduction. The structure analysis of the title compound was undertaken as part of our systematic investigation of bridged diketones (Sinha *et al.*, 1983).



Conformational analysis of various non-aromatic rings (Geise, Altona & Romers, 1967) in some steroid structures showed that ring *C* assumed a distorted chair configuration, ring *B* varied from half-chair to sofa while ring *D* varied from envelope to intermediate between envelope and half-chair (Altona, Geise & Romers, 1968). In the present paper the results obtained for the title compound, notably of the geometry of the *B, C, D* moiety, are compared with those for the *cis*-bridged diketone reported in the preceding paper (Mukherjee & Mukherjee, 1984).

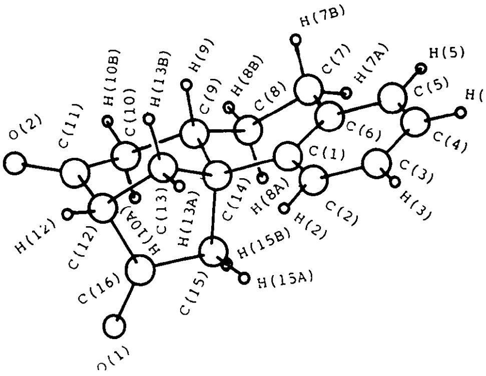


Fig. 1. Perspective view of the molecule along **b** with the atom numbering scheme.

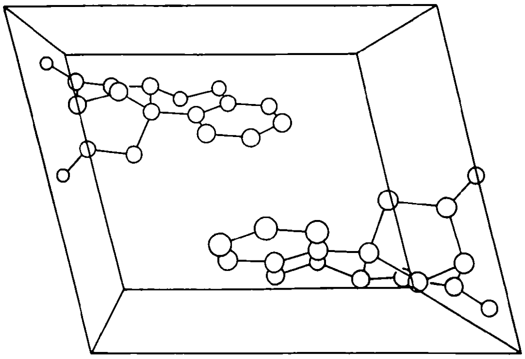


Fig. 2. Packing diagram, viewed as in Fig. 1; *a* points down the page, *c* to the left.

Table 1. *Positional parameters* ($\times 10^4$ *for* C, O; $\times 10^3$ *for* H) *and isotropic thermal parameters* (Å^2 $\times 10$) *with e.s.d.'s in parentheses*

The atomic labelling of the H atoms refers to that of the C atoms to which they are bonded.

	x	y	z	B_{eq}/B_{iso}*
C(1)	2760 (5)	3483	−3939 (4)	29 (2)
C(2)	3504 (5)	5189 (7)	−4066 (4)	37 (2)
C(3)	3683 (6)	5801 (8)	−5264 (5)	48 (2)
C(4)	3107 (6)	4705 (10)	−6365 (5)	64 (3)
C(5)	2410 (6)	3011 (10)	−6250 (4)	48 (3)
C(6)	2232 (5)	2369 (7)	−5047 (4)	34 (2)
C(7)	1497 (6)	461 (8)	−4989 (4)	43 (2)
C(8)	1850 (6)	−328 (7)	−3605 (5)	39 (2)
C(9)	1449 (5)	1197 (7)	−2707 (4)	32 (2)
C(10)	1384 (6)	395 (8)	−1369 (5)	43 (2)
C(11)	1336 (6)	1870 (8)	−369 (4)	43 (2)
C(12)	2370 (6)	3569 (7)	−417 (4)	38 (2)
C(13)	1941 (5)	4397 (7)	−1818 (4)	34 (2)
C(14)	2600 (5)	2883 (7)	−2591 (4)	28 (2)
C(15)	4253 (5)	2458 (7)	−1667 (4)	36 (2)
C(16)	4041 (5)	2838 (8)	−307 (4)	36 (2)
O(1)	5050 (4)	2614 (6)	707 (3)	50 (2)
O(2)	588 (5)	1709 (7)	453 (4)	69 (2)
H(2)	395 (6)	586 (8)	−328 (5)	34 (12)
H(3)	425 (6)	689 (10)	−534 (5)	44 (14)
H(4)	329 (7)	500 (10)	−720 (5)	55 (15)
H(5)	199 (6)	225 (7)	−704 (4)	23 (11)
H(7*A*)	190 (6)	−38 (9)	−557 (5)	43 (13)
H(7*B*)	28 (6)	48 (9)	−537 (5)	35 (13)
H(8*A*)	304 (6)	−62 (7)	−329 (4)	25 (11)
H(8*B*)	117 (6)	−137 (8)	−358 (5)	38 (13)
H(9)	32 (5)	157 (7)	−314 (4)	17 (10)
H(10*A*)	241 (5)	−48 (7)	−101 (4)	15 (10)
H(10*B*)	44 (6)	−48 (8)	−149 (5)	28 (11)
H(12)	228 (6)	457 (9)	26 (5)	36 (12)
H(13*A*)	252 (5)	553 (7)	−186 (4)	20 (10)
H(13*B*)	73 (5)	464 (7)	−218 (4)	24 (11)
H(15*A*)	510 (5)	331 (7)	−184 (4)	11 (9)
H(15*B*)	465 (5)	121 (7)	−175 (4)	19 (10)

* $B_{eq} = \frac{1}{3}\sum_i B_{ii}$ for non-hydrogen atoms.

Experimental. Crystals supplied by Professor U. R. Ghatak, IACS, Calcutta; cell parameters derived from least-squares refinement of 25 randomly chosen reflections; intensity data for 1216 reflections collected, 0·32 × 0·30 × 0·10 mm crystal, $2 \leq \theta \leq 25°$, Enraf–Nonius CAD-4 diffractometer, ω–2θ scans, graphite-monochromated Mo $K\alpha$ radiation, no crystal decomposition during data collection, no correction for absorption; 1080 reflections $[F_o > 2\sigma(F_o)]$ used in analysis, index range h −10–9, k 0–8, l 0–12; structure solved by *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), positions of H atoms fixed from standard geometry, block-diagonal least-squares refinement (Vickery, Bright & Mallinson, 1971), anisotropic for non-H atoms and isotropic for H atoms, $R = 0{\cdot}044$, $wR = 0{\cdot}064$ for the 1080 observed reflections; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F)$; for $|F_o| \leq 9{\cdot}1$, $\sigma(F) = 0{\cdot}41\,|F_o|$; for $9{\cdot}1 < |F_o| \leq 12{\cdot}5$, $\sigma(F) = 0{\cdot}30\,|F_o|$; for $12{\cdot}5 < |F_o| \leq 19{\cdot}2$, $\sigma(F) = 0{\cdot}24\,|F_o|$; for $19{\cdot}2 < |F_o| \leq 29{\cdot}9$, $\sigma(F) = 0{\cdot}16\,|F_o|$; for $29{\cdot}9 < |F_o| \leq 41{\cdot}0$, $\sigma(F) = 0{\cdot}12\,|F_o|$; for $|F_o| > 41{\cdot}0$, $\sigma(F) = 0{\cdot}05\,|F_o|$ (Seal & Ray, 1981); in final refinement cycle max. Δ/σ for non-H atoms 0·58, for H atoms, 1·46; residual electron density in final difference Fourier map $\pm 0{\cdot}2$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray*

Table 2. *Bond distances* (Å), *bond angles* (°) *and comparison of torsion angles* (°) *for rings B, C and D in trans- and cis-bridged diketones* (*Mukherjee & Mukherjee*, 1984)

C(1)–C(2)	1·402 (5)	C(1)–C(6)	1·397 (5)
C(2)–C(3)	1·383 (7)	C(3)–C(4)	1·390 (8)
C(4)–C(5)	1·372 (9)	C(5)–C(6)	1·394 (6)
C(6)–C(7)	1·514 (7)	C(7)–C(8)	1·527 (6)
C(8)–C(9)	1·540 (6)	C(9)–C(14)	1·550 (6)
C(1)–C(14)	1·524 (5)	C(9)–C(10)	1·538 (6)
C(10)–C(11)	1·501 (7)	C(11)–C(12)	1·517 (7)
C(12)–C(13)	1·552 (6)	C(13)–C(14)	1·547 (6)
C(14)–C(15)	1·551 (6)	C(12)–C(16)	1·513 (6)
C(15)–C(16)	1·515 (6)	C(16)–O(1)	1·215 (5)
C(11)–O(2)	1·207 (6)		
C(1)–C(2)–C(3)	121·3 (4)	C(2)–C(3)–C(4)	119·3 (5)
C(3)–C(4)–C(5)	120·0 (5)	C(4)–C(5)–C(6)	121·4 (5)
C(5)–C(6)–C(1)	119·2 (4)	C(6)–C(1)–C(2)	118·8 (4)
C(1)–C(6)–C(7)	122·4 (4)	C(6)–C(7)–C(8)	112·6 (4)
C(7)–C(8)–C(9)	107·7 (4)	C(8)–C(9)–C(14)	111·4 (4)
C(9)–C(14)–C(1)	110·4 (3)	C(6)–C(1)–C(14)	122·3 (4)
C(14)–C(9)–C(10)	112·6 (4)	C(9)–C(10)–C(11)	113·4 (4)
C(10)–C(11)–C(12)	115·0 (4)	C(11)–C(12)–C(13)	109·4 (4)
C(12)–C(13)–C(14)	101·6 (3)	C(13)–C(14)–C(9)	106·0 (3)
C(13)–C(14)–C(15)	101·9 (3)	C(14)–C(15)–C(16)	104·8 (4)
C(15)–C(16)–C(12)	108·8 (4)	C(13)–C(12)–C(16)	102·0 (4)
C(12)–C(16)–O(1)	125·4 (4)	C(15)–C(16)–O(1)	125·7 (4)
C(10)–C(11)–O(2)	123·3 (5)	C(12)–C(11)–O(2)	121·6 (5)
Ring *B*		*trans* diketone	*cis* diketone
C(8)–C(9)–C(14)–C(1)		47·8 (5)	62·0 (5)
C(7)–C(8)–C(9)–C(14)		−66·9 (5)	−52·0 (5)
C(6)–C(7)–C(8)–C(9)		49·3 (5)	15·7 (6)
C(1)–C(6)–C(7)–C(8)		−17·0 (6)	9·3 (6)
C(14)–C(1)–C(6)–C(7)		−1·7 (6)	2·1 (8)
C(9)–C(14)–C(1)–C(6)		−13·7 (6)	−35·8 (6)
Ring *C*			
C(11)–C(12)–C(13)–C(14)		−69·9 (4)	37·4 (6)
C(10)–C(11)–C(12)–C(13)		54·1 (5)	−41·7 (6)
C(9)–C(10)–C(11)–C(12)		−38·5 (5)	60·1 (5)
C(14)–C(9)–C(10)–C(11)		42·1 (5)	−70·5 (5)
C(13)–C(14)–C(9)–C(10)		−61·2 (5)	69·3 (5)
C(12)–C(13)–C(14)–C(9)		72·8 (4)	−53·9 (6)
Ring *D*			
C(14)–C(15)–C(16)–C(12)		−3·3 (6)	−7·3 (6)
C(15)–C(16)–C(12)–C(13)		−24·1 (5)	−21·8 (5)
C(16)–C(12)–C(13)–C(14)		42·1 (5)	41·9 (6)
C(12)–C(13)–C(14)–C(15)		−44·4 (5)	−47·5 (4)
C(13)–C(14)–C(15)–C(16)		29·6 (5)	33·6 (5)

Crystallography (1974); all computations performed on the Burroughs B6700 computer at the Regional Computer Centre, Jadavpur University Campus, Calcutta.

Discussion. Final atomic parameters, bond distances and angles and selected torsion angles are given in Tables 1 and 2.* A perspective view of the molecule with the atom-numbering scheme and a packing diagram are shown in Figs. 1 and 2. Analysis of these data clearly establishes that the *B*/*C* junction is *trans* (Bucourt, 1974).

The phenyl ring is essentially planar. Ring *B* assumes a distorted half-chair conformation in contrast to the half-boat conformation in the *cis*-bridged diketone (Mukherjee & Mukherjee, 1984). The degree of distortion can be seen from the torsion angles listed in Table 2. The sum of the ring *B* torsion angles is 196 (3)°, compared with 335° for a normal cyclohexane ring (Gabe, Lee & Boudreau, 1982). A considerably distorted chair conformation is adopted by ring *C* [torsion angles in range 38·5 (5)–72·8 (4)°, sum 339 (3)°]. Unlike the *cis*-bridged diketone, which has ring *D* geometry intermediate between envelope and half-chair, the conformation of ring *D* in the present case, with a maximum torsion angle 44·4 (5)°, is a slightly distorted envelope. The structure shows considerable strain with formally tetrahedral C—C—C valence angles varying from 102 to 115°, the greatest distortion being in the five-membered ring. This can be understood in terms of conformational transmission effects (Barton, 1970). The crystal structure consists of discrete molecules with no intermolecular distance shorter than the sum of the van der Waals radii (Pauling, 1960).

The authors wish to thank Professor U. R. Ghatak and Dr S. Ray, IACS, Calcutta, for supplying the title compound and helpful discussions, and Dr S. Roy, RCC, Calcutta, for encouragement and assistance with the computation.

References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

BARTON, D. H. R. (1970). *Science*, **169**, 539–544.

BUCOURT, R. (1974). *Topics in Stereochemistry*, Vol. 8, edited by E. L. ELIEL & N. L. ALLINGER, pp. 159–224. New York: John Wiley.

GABE, E. J., LEE, F. L. & BOUDREAU, S. M. (1982). *Acta Cryst.* B**38**, 2975–2977.

GEISE, H. J., ALTONA, C. & ROMERS, C. (1967). *Tetrahedron*, **23**, 439–463.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MUKHERJEE, A. K. & MUKHERJEE, M. (1984). *Acta Cryst.* C**40**, 981–983.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

SEAL, A. & RAY, S. (1981). *Indian J. Phys.* **55**A, 414–416.

SINHA, G., MAJI, S. K., GHATAK, U. R., MUKHERJEE, M., MUKHERJEE, A. K. & CHAKRAVORTY, A. K. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 2519–2528.

VICKERY, B. L., BRIGHT, D. & MALLINSON, P. R. (1971). *XRAY ARC.* IBM 1130 program system for crystallography modified for the Burroughs B6700 computer.

---

* Lists of structure amplitudes, anisotropic thermal parameters, least-squares plane calculations and bond lengths involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39139 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.