

alanine monohydrate are also very similar to those of three other model therapeutic agents for the treatment of sickle-cell disease (Wang & Burley, 1987*a,b*; Fujii, Burley & Wang, 1987). These structures are stabilized by a weakly polar interaction, which results from the characteristic segregation of partial charges in aromatic moieties (Burley & Petsko, 1986). A mechanism of antisickling action has been proposed by Burley, Wang, Votano & Rich (1987).

I thank Professor G. A. Petsko for his encouragement, and acknowledge the support of a W. R. Grace Foundation research fellowship. Finally, I thank Drs J. C. Dewan and J. Troup for data collection.

References

- BURLEY, S. K. & PETSKO, G. A. (1986). *J. Am. Chem. Soc.* **108**, 7995–8001.
- BURLEY, S. K. & WANG, A. H.-J. (1987). *Acta Cryst.* **C43**, 797–799.
- BURLEY, S. K., WANG, A. H.-J., VOTANO, J. R. & RICH, A. (1987). *Biochemistry*, **25**. In the press.
- FUJII, S., BURLEY, S. K. & WANG, A. H.-J. (1987). *Acta Cryst.* **C43**, 1008–1009.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–75. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.
- JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, 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.
- RAMACHANDRAN, G. N., COLASKAR, D., RAMAKRISHNAN, C. & SASISEKHARAN, V. (1974). *Biochim. Biophys. Acta*, **359**, 298–317.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WANG, A. H.-J. & BURLEY, S. K. (1987*a*). *Acta Cryst.* **C43**, 1011–1012.
- WANG, A. H.-J. & BURLEY, S. K. (1987*b*). *Acta Cryst.* **C43**, In the press.

Acta Cryst. (1987). **C43**, 1318–1320

Structure of an Intermediate Related to a Steroid

BY APURBA KABIRAJ AND SUNDAR GOPAL BISWAS*

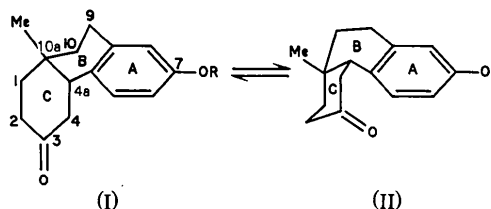
Physics Department, Visva-Bharati University, West Bengal, Pin-731235, India

(Received 14 October 1986; accepted 7 January 1987)

Abstract. 1,2,3,4,4a,9,10,10a-Octahydro-7-methoxy-10a β -methyl-(4a β H)-3-oxophenanthrene, $C_{16}H_{20}O_2$, $M_r=244.33$, monoclinic, $P2_1/c$, $a=9.922(2)$, $b=8.642(2)$, $c=16.068(2)$ Å, $\beta=100.29(1)^\circ$, $V=1355.6(5)$ Å³, $Z=4$, $D_x=1.20$ g cm⁻³, $\lambda(Cu K\alpha)=1.5418$ Å, $\mu(Cu K\alpha)=6.18$ cm⁻¹, $F(000)=528$, room temperature, $R=0.043$ for 1705 reflections. The ring junction is *cis*-fused between two six-membered rings and the ring-fusion methyl carbon atom is axial to the *B* ring. The unsaturated six-membered ring of the molecule is substantially planar while the other two saturated six-membered rings are respectively in chair and half-chair conformations.

Introduction. The presence of partially aromatized hydrocarbons related to steroids has been noticed in geological samples and the first identification of one type has been reported (Schaeffe, Ludwig, Albrecht & Ourison, 1978). In connection with the total synthesis of this partially aromatized hydrocarbon and related

compounds, a stereospecific *cis*-reduction of a hydrophenanthrene derivative yielded the title compound, a *B/C-cis* ketone, as an intermediate (Chatterjee, Chaudhury & Chatterjee, 1982). It is suggested that compounds having this type of *B/C-cis* configuration usually equilibrate between two conformers, where the ring-fusion methyl carbon and hydrogen atoms may be axial and equatorial respectively to the *B* ring (I) or *vice versa* (II), owing to the flexible nature of the rings. An X-ray diffraction study of this ketone has been undertaken to confirm the stereospecificity of this *cis* reduction as well as to determine its three-dimensional molecular structure.



* Author to whom correspondence should be addressed.

Experimental. Crystallized from petroleum ether solution as transparent colourless octahedron-like crystal, Syntex $P2_1$ four-circle diffractometer, unit-cell parameters by least-squares calculations from angular setting of 15 independent reflections, $10 \leq \theta \leq 17^\circ$, graphite-monochromatized $\text{Cu K}\alpha$ radiation, crystal $0.25 \times 0.22 \times 0.18$ mm, ω -scan technique; $2\theta \leq 114^\circ$, $10 \geq h \geq 0$, $9 \geq k \geq 0$, $16 \geq l \geq -17$; 1830 unique reflections measured, 1705 observed with $F_o \geq 4\sigma(F_o)$, no absorption or extinction corrections, observed systematic absences indicated $P2_1/c$, intensity of one standard reflection measured after every 50 reflections, no systematic or significant variation of intensity.

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

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O(1)	−3249 (1)	1722 (2)	6417 (1)	5.09 (4)
O(2)	3101 (2)	8516 (2)	6179 (1)	6.24 (5)
C(1)	−1999 (2)	2402 (2)	6419 (1)	3.92 (5)
C(2)	−1026 (2)	1876 (2)	5969 (1)	3.93 (5)
C(3)	232 (2)	2627 (2)	6017 (1)	3.60 (5)
C(4)	524 (2)	3925 (2)	6532 (1)	3.61 (5)
C(5)	−478 (2)	4439 (2)	6981 (1)	4.40 (5)
C(6)	−1714 (2)	3706 (2)	6929 (1)	4.64 (6)
C(7)	1263 (2)	1960 (2)	5526 (1)	4.44 (6)
C(8)	2491 (2)	3011 (2)	5509 (1)	4.56 (6)
C(9)	3021 (2)	3762 (2)	6366 (1)	4.04 (5)
C(10)	1874 (2)	4784 (2)	6607 (1)	3.74 (5)
C(11)	1657 (2)	6296 (2)	6089 (1)	4.64 (6)
C(12)	2960 (2)	7152 (2)	6038 (1)	4.89 (6)
C(13)	4073 (2)	6169 (3)	5789 (2)	5.66 (7)
C(14)	4305 (2)	4747 (3)	6348 (1)	5.20 (6)
C(15)	3411 (2)	2522 (3)	7039 (2)	5.38 (6)
C(16)	−3548 (2)	345 (3)	5937 (1)	5.52 (6)

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

C(1)–O(1)	1.371 (2)	C(1)–C(2)	1.383 (3)
C(1)–C(6)	1.392 (3)	C(2)–C(3)	1.396 (3)
C(3)–C(4)	1.394 (3)	C(3)–C(7)	1.514 (3)
C(4)–C(5)	1.401 (3)	C(4)–C(10)	1.517 (3)
C(5)–C(6)	1.370 (3)	C(7)–C(8)	1.524 (3)
C(8)–C(9)	1.527 (3)	C(9)–C(10)	1.545 (3)
C(9)–C(14)	1.538 (3)	C(9)–C(15)	1.523 (3)
C(10)–C(11)	1.544 (3)	C(11)–C(12)	1.504 (3)
C(12)–C(13)	1.504 (3)	C(12)–O(2)	1.204 (2)
C(13)–C(14)	1.515 (3)	C(16)–O(1)	1.421 (3)
C(1)–O(1)–C(16)	117.5 (2)	O(1)–C(1)–C(6)	115.9 (2)
O(1)–C(1)–C(2)	125.0 (2)	C(2)–C(1)–C(6)	119.1 (2)
C(1)–C(2)–C(3)	121.3 (2)	C(2)–C(3)–C(7)	118.4 (2)
C(2)–C(3)–C(4)	119.7 (2)	C(4)–C(3)–C(7)	121.8 (2)
C(3)–C(4)–C(10)	121.9 (2)	C(3)–C(4)–C(5)	118.0 (2)
C(5)–C(4)–C(10)	120.1 (2)	C(4)–C(5)–C(6)	122.1 (2)
C(1)–C(6)–C(5)	119.7 (2)	C(3)–C(7)–C(8)	113.5 (2)
C(7)–C(8)–C(9)	112.6 (2)	C(8)–C(9)–C(15)	110.2 (2)
C(8)–C(9)–C(14)	111.8 (2)	C(8)–C(9)–C(10)	108.6 (2)
C(14)–C(9)–C(15)	107.3 (2)	C(10)–C(9)–C(15)	109.2 (2)
C(10)–C(9)–C(14)	109.8 (2)	C(4)–C(10)–C(9)	112.3 (2)
C(9)–C(10)–C(11)	112.7 (2)	C(4)–C(10)–C(11)	109.6 (2)
C(10)–C(11)–C(12)	114.1 (2)	O(2)–C(12)–C(11)	122.9 (2)
C(11)–C(12)–C(13)	114.6 (2)	O(2)–C(12)–C(13)	122.5 (2)
C(12)–C(13)–C(14)	110.0 (2)	C(9)–C(14)–C(13)	114.9 (2)

Table 3. Selected torsional angles ($^\circ$) with e.s.d.'s in parentheses

I			
C(2)–C(1)–C(6)–C(5)	–0.4 (3)	C(1)–C(2)–C(3)–C(4)	0.5 (3)
C(2)–C(3)–C(4)–C(5)	–0.6 (3)	C(3)–C(4)–C(5)–C(6)	0.2 (3)
C(4)–C(5)–C(6)–C(1)	0.3 (3)	C(6)–C(1)–C(2)–C(3)	0.0 (3)
II			
C(4)–C(3)–C(7)–C(8)	–11.7 (3)	C(7)–C(3)–C(4)–C(10)	2.2 (3)
C(7)–C(8)–C(9)–C(10)	–61.8 (2)	C(8)–C(9)–C(10)–C(4)	50.5 (2)
C(3)–C(4)–C(10)–C(9)	–22.4 (3)	C(3)–C(7)–C(8)–C(9)	42.0 (2)
III			
C(9)–C(10)–C(11)–C(12)	–47.5 (2)	C(10)–C(11)–C(12)–C(13)	49.2 (3)
C(11)–C(12)–C(13)–C(14)	–51.5 (3)	C(12)–C(13)–C(14)–C(9)	55.2 (3)
C(10)–C(9)–C(14)–C(13)	–54.3 (3)	C(14)–C(9)–C(10)–C(11)	48.6 (2)
IV			
C(15)–C(9)–C(10)–C(11)	165.9 (2)	C(15)–C(9)–C(14)–C(13)	–172.8 (3)
C(7)–C(8)–C(9)–C(15)	57.8 (2)	C(15)–C(9)–C(10)–C(4)	–69.7 (2)
V			
C(3)–C(4)–C(10)–H(10)	–140 (1)	C(8)–C(9)–C(10)–H(10)	170 (1)
H(10)–C(10)–C(11)–C(12)	69 (1)	C(14)–C(9)–C(10)–H(10)	–68 (1)

Structure solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), some H atoms were located from difference Fourier map and the rest generated; isotropic and anisotropic refinement of H and non-H atoms respectively by block-diagonal least-squares method gave final $R = 0.043$ and $wR = 0.05$, function $\sum(w|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F)$, $\sigma(F)$ standard deviation in the observed amplitude derived from counting statistics, maximum shift/e.s.d. ratios are 0.7 and 1.42 for non-H and H atoms respectively, maximum height in final difference Fourier map 0.25 and largest hole -0.28 e \AA^{-3} , atomic scattering factors from *International Tables for X-ray Crystallography* (1974), program *XRAY ARC* (Vickery, Bright & Mallinson, 1973) modified for the B6700 computer.

Discussion. Final atomic parameters, bond distances and angles and selected torsion angles with their e.s.d.'s are given in Tables 1, 2 and 3 respectively. The molecular structure projected along the *c* axis with the atomic numbering scheme is given in Fig. 1.*

The derived stereochemistry of the molecule reveals that its *A* ring is substantially planar whereas the *B* and *C* rings assume a half-chair and chair conformation respectively. The torsion angles (Table 3) indicate the degree of distortion as well as other stereochemical features. Torsion angles of the same sign about the C(9)–C(10) bond for rings *B* and *C*, C(8)–C(9)–C(10)–C(4) and C(14)–C(9)–C(10)–C(11) [$+50.5$ (2) and $+48.6$ (2) $^\circ$ respectively], confirm the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43708 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

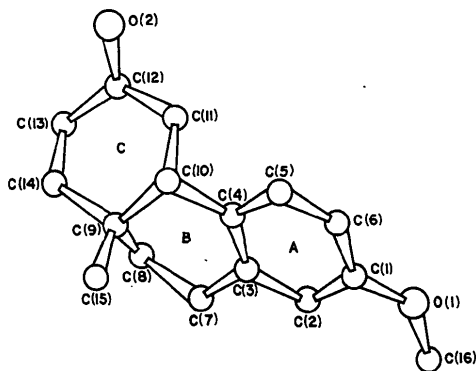


Fig. 1. The view of the molecule projected along the *c* axis.

stereospecificity of the reduction process, *i.e.* the formation of a *cis* ketone (Bucourt, 1974). The ring-fusion methyl group is axial to the *B* ring and equatorial to the ketone-containing *C* ring of the molecule and the ring-fusion hydrogen atom is equatorial to the *B* ring and axial to ring *C*. The calculated distance of 2.67 Å between the H atom attached to aromatic C(5) and that attached to C(1) of the *A* ring coincides with the computed distance (from a Dreiding model) of 2.7 Å between these hydrogen atoms in one of the *cis* models (Nagata, Terasawa & Tori, 1964) that is in the ground state. The crystal structure consists of discrete molecules with no intermolecular distance shorter than van der Waals radii (Pauling, 1960).

The authors sincerely acknowledge the kind help of Professor G. Germain, Department of Quantum Chemistry, Catholic University of Louvain, Belgium, who collected the diffraction data for us. The authors also offer sincere thanks to Professor A. Chatterjee, Jadavpur University, Calcutta, for his helpful discussion on the conformation of the title compound which was synthesized in his laboratory and to Dr S. Roy of IACS, Calcutta, for his help in solving some of the computational problems.

References

- BUCOURT, R. (1974). *Topics in Stereochemistry*, Vol. 8, edited by E. L. ELIEL & N. L. ALLINGER, pp. 159–224. New York: John Wiley.
- CHATTERJEE, A., CHAUDHURY, S. R. R. & CHATTERJEE, S. K. (1982). *J. Chem. Soc. Chem. Commun.* 1, 24–25.
- International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERQ, 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.
- NAGATA, N., TERASAWA, T. & TORI, K. (1964). *J. Am. Chem. Soc.* **86**, 3746–3749.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- SCHAEFLE, J., LUDWIG, B., ALBRECHT, P. & OURISSON, G. (1978). *Tetrahedron Lett.* **43**, 4163–4166.
- VICKERY, E. L., BRIGHT, D. & MALLINSON, P. R. (1971). *XRAY ARC*. IBM 1130 program system for crystallography modified for the Burroughs B6700 computer.

Acta Cryst. (1987). **C43**, 1320–1322

3,6-Diamino-1,2,4,5-tetrazine: An Example of Strong Intermolecular Hydrogen Bonding

BY CLAUS KRIEGER, HANS FISCHER AND FRANZ A. NEUGEBAUER*

Max-Planck-Institut für medizinische Forschung, Abteilung Organische Chemie, Jahnstrasse 29, D-6900 Heidelberg, Federal Republic of Germany

(Received 19 November 1986; accepted 9 February 1987)

Abstract. C₂H₄N₆, *M_r* = 112.1, orthorhombic, *Amam*, *a* = 6.257 (1), *b* = 7.839 (1), *c* = 9.424 (1) Å, *V* = 462.2 (2) Å³, *Z* = 4, *D_x* = 1.611 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.1160 mm⁻¹, *F*(000) = 232, room temperature, final conventional *R* = 0.038 for 260 unique observed reflections. The crystal-structure analysis confirms the 3,6-diamino-1,2,4,5-tetrazine structure. The amino groups act as proton donors forming intermolecular hydrogen bonds with adjacent

N atoms of neighbouring 1,2,4,5-tetrazine rings. The intermolecular hydrogen-bonding network leads to planar molecular layers separated from each other by $\frac{1}{2}a$ [3.129 (1) Å].

Introduction. In the context of detailed studies of 3,6-disubstituted 1,2,4,5-tetrazines some unusual properties of the title compound (1a) (Lin, Lieber & Horowitz, 1954) attracted attention, *e.g.* the unexpectedly high first ionization potential in the photoelectron spectrum (Gleiter, Spanget-Larsen, Fischer &

* To whom correspondence should be addressed.