the two C–C in the ketone bridge is 1·505 Å; these bonds should be shorter since each involves the trigonal bridgehead C atom.

The bicyclic system shows a chair–boat conformation as can be deduced from the torsion angles (Table 3) and the deposited conformational parameters (Cano, Foces-Foces & García-Blanco, 1977). Both rings are very near an ideal conformation and they have dominant mirror symmetry [C_s plane through N(3), N(7), C(9), O(1), C(17)].

Table 2. *Bond lengths* (Å) *and valence angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·549 (3)	N(7)–C(8)	1·396 (4)
C(1)–C(8)	1·536 (3)	N(7)–C(17)	1·469 (3)
C(1)–C(9)	1·500 (3)	C(9)–O(1)	1·217 (3)
C(2)–N(3)	1·463 (3)	C(10)–C(11)	1·514 (4)
N(3)–C(4)	1·458 (3)	C(11)–C(12)	1·378 (3)
N(3)–C(10)	1·472 (3)	C(11)–C(16)	1·384 (3)
C(4)–C(5)	1·532 (3)	C(12)–C(13)	1·396 (4)
C(5)–C(6)	1·540 (3)	C(13)–C(14)	1·373 (4)
C(5)–C(9)	1·511 (3)	C(14)–C(15)	1·380 (4)
C(6)–N(7)	1·464 (3)	C(15)–C(16)	1·390 (3)
C(8)–C(1)–C(9)	108·6 (2)	C(8)–N(7)–C(17)	110·5 (2)
C(2)–C(1)–C(9)	106·0 (2)	C(1)–C(8)–N(7)	109·9 (2)
C(2)–C(1)–C(8)	112·6 (2)	C(1)–C(9)–C(5)	110·7 (2)
C(1)–C(2)–N(3)	110·4 (2)	C(5)–C(9)–O(1)	124·3 (2)
C(2)–N(3)–C(10)	110·0 (2)	C(1)–C(9)–O(1)	124·8 (2)
C(2)–N(3)–C(4)	111·2 (2)	N(3)–C(10)–C(11)	112·9 (2)
C(4)–N(3)–C(10)	111·8 (2)	C(10)–C(11)–C(16)	120·6 (2)
N(3)–C(4)–C(5)	110·3 (2)	C(10)–C(11)–C(12)	120·6 (2)
C(4)–C(5)–C(9)	106·4 (2)	C(12)–C(11)–C(16)	118·8 (2)
C(4)–C(5)–C(6)	112·3 (2)	C(11–C(12)–C(13)	120·8 (2)
C(6)–C(5)–C(9)	108·2 (2)	C(12)–C(13)–C(14)	120·0 (3)
C(5)–C(6)–N(7)	110·0 (2)	C(13)–C(14)–C(15)	119·7 (2)
C(6)–N(7)–C(17)	110·9 (2)	C(14)–C(15)–C(16)	120·2 (2)
C(6)–N(7)–C(8)	110·4 (2)	C(11)–C(16)–C(15)	120·5 (2)

Table 3. *Torsion angles* (°)

C(8)–C(1)–C(9)–C(5)	−58·9 (2)	C(2)–N(3)–C(4)–C(5)	−60·1 (2)
C(1)–C(9)–C(5)–C(6)	58·0 (2)	N(3)–C(4)–C(5)–C(9)	59·8 (2)
C(9)–C(5)–N(7)	1·9 (2)	C(4)–C(5)–C(9)–C(1)	−62·9 (2)
C(5)–C(6)–N(7)–C(8)	−61·8 (2)	C(5)–C(9)–C(1)–C(2)	62·4 (2)
C(6)–N(7)–C(8)–C(1)	61·0 (2)	C(4)–N(3)–C(10)–C(11)	−63·8 (2)
N(7)–C(8)–C(1)–C(9)	−0·4 (6)	C(2)–N(3)–C(10)–C(11)	172·2 (2)
C(9)–C(1)–C(2)–N(3)	−59·5 (2)	N(3)–C(10)–C(11)–C(12)	129·8 (2)
C(1)–C(2)–N(3)–C(4)	59·9 (2)	N(3)–C(10)–C(11)–C(16)	−52·7 (3)

None of the intermolecular distances is less than a normal van der Waals contact. The closest approach is 3·350 Å and is that of the O of one molecule to C(16) of a molecule related to the first by symmetry of type $x,y,z+1$.

We thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia (Madrid) for the use of the 1108 Univac computer.

References

CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Tetrahedron*, **33**, 797–802.

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

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L. GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN* 80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1983). C**39**, 103–105

Structure of 1,3,9,9,10,10-Hexamethyl-2,4,6,8-tetraoxatricyclo[3.3.1.1^{3,7}]decane, $C_{12}H_{20}O_4$

BY SETSUO KASHINO AND MASAO HAISA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, *Japan*

AND SADAO TSUBOI, TSUYOSHI ONO AND AKIRA TAKEDA

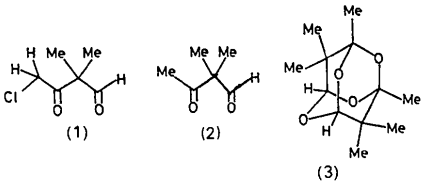
Department of Synthetic Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700, *Japan*

(*Received* 9 *June* 1982; *accepted* 22 *July* 1982)

Abstract. $M_r = 228·29$, orthorhombic, *Pbna*, $a = 11·043$ (1), $b = 15·847$ (1), $c = 6·764$ (1) Å, $V = 1183·6$ (2) Å^3, $Z = 4$, $D_m = 1·24$, $D_x = 1·281$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·74$ mm^{-1}, $F(000) = 496$; the final $R = 0·052$ for 853 non-zero reflexions. The molecule retains twofold symmetry in the crystals. The tetraoxaadamantane skeleton reveals no significant distortion. The average dimensions are: O–C 1·426 (2), C–C 1·536 (3) Å; O–C–O 110·2 (2), C–O–C 111·5 (2)°.

0108-2701/83/010103-03$01.50

Introduction. For the mechanistic study of a new type of Favorskii rearrangement, 4-chloro-2,2-dimethyl-3-oxobutanal (1) was required. Attempted reaction of 2,2-dimethyl-3-oxobutanal (2) with sulfuryl chloride to obtain (1), however, afforded a substance which (based on MS and ^{13}C NMR spectra) is supposed to be either the structural isomer of (2) or the dimer, the title compound (3). The present study has been made in order to determine the structure, and has confirmed that the substance is (3) and has a tetraoxaadamantane skeleton. There has been no previous X-ray crystallographic study of this skeleton.



Experimental. (3) synthesized in quantitative yield from (2) by treatment with sulfuryl chloride in carbon tetrachloride for 3 h at room temperature, m.p. 352–353 K (lit. 351–352 K, Almqvist, 1968); ^{13}C NMR ($CDCl_3$): δ 20·5 (q, CH_3), 20·7 (q, CH_3), 21·1 (q, CH_3), 36·9 [s, C(9) and C(10)], 100·2 [d, C(5) and C(7)], 102·2 p.p.m. [s, C(1) and C(3)]; IR and ^1H NMR spectral data identical with those in the literature for (3) (Almqvist, 1968); colorless plates (slow evaporation from hexane), developed faces {010}, bounded by {101}, density measured in aqueous KI by flotation, systematic absences $0kl$ for k odd, $h0l$ for $h+l$ odd, $hk0$ for h odd; since crystals sublimed gradually, a specimen 0·35 × 0·08 × 0·28 mm was sealed in a glass capillary, Rigaku AFC-5 four-circle diffractometer, lattice parameters determined from 14 reflexions by least-squares calculations, intensities measured to $2\theta = 120°$, ω–2θ scan method [scan speed 4° min^{-1} (2θ); scan range (2θ): 1·2° + 0·15°tanθ], Ni-filtered Cu $K\alpha$ radiation, 40 kV, 200 mA, background measured for 4 s on either side of the peak, three reference reflexions showed no intensity deterioration, Lorentz and polarization corrections, no absorption correction; 882 independent reflexions collected, 853 non-zero reflexions [$|F_o| > \sigma(F)$] used in the refinement; structure solved by *MULTAN*, refined (non-H atoms anisotropic) by block-diagonal least-squares method, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1·0$ for $0 < |F_o| \leq 12·0$ and $(12·0/|F_o|)^2$ for $|F_o| > 12·0$, H-atom positions determined from a difference synthesis and refined (isotropically) by the least-squares method; extinction correction applied for the three strongest reflexions [$I_{corr} = I_{obs}\ (1 - 3·0 \times 10^{-5} I_{obs})$]; final $wR = 0·061$, $S = 0·512$; maximum shifts in final refinement cycle for non-H and H atoms were $0·25\sigma$ and $0·8\sigma$, respectively, maximum and minimum heights in the final difference Fourier synthesis were ±0·30 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at Okayama University Computer Center; programs *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *HBLS*-V (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1965).

Discussion. The final atomic parameters are listed in Table 1.* A stereoview of the molecule with atomic numbering is shown in Fig. 1. Bond lengths and angles are given in Table 2. A projection of the crystal structure viewed along **c** is shown in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving the H atoms, the least-squares planes and displacements of the atoms from the planes, and endocyclic and exocyclic torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38091 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic parameters (positional* $\times 10^4$*, for* H $\times 10^3$*) with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3} \sum_i \beta_{ii} / a_i^{*2}$.

	x	y	z	B_{eq} or B_{iso}(Å^2)
O(1)	351 (1)	2500	5000	2·74 (7)
O(2)	3351 (2)	2500	5000	3·28 (8)
O(3)	1859 (1)	1989 (1)	7128 (2)	3·03 (6)
C(4)	1062 (2)	1780 (1)	5522 (3)	2·74 (8)
C(5)	1839 (2)	1527 (1)	3726 (3)	2·79 (8)
C(6)	2610 (2)	2313 (1)	3341 (3)	2·96 (8)
C(7)	189 (2)	1132 (1)	6304 (3)	3·94 (9)
C(8)	2658 (2)	771 (1)	4185 (3)	3·93 (9)
C(9)	1074 (2)	1332 (1)	1899 (3)	3·83 (9)
H(6)	315 (2)	224 (1)	216 (3)	1·9 (5)
H(7*A*)	56 (2)	66 (2)	677 (3)	3·7 (6)
H(7*B*)	−20 (2)	136 (1)	749 (4)	3·0 (5)
H(7*C*)	−37 (2)	97 (2)	522 (4)	4·4 (6)
H(8*A*)	303 (2)	81 (2)	538 (4)	3·4 (6)
H(8*B*)	221 (2)	22 (1)	415 (3)	3·1 (5)
H(8*C*)	324 (3)	70 (2)	302 (4)	4·5 (7)
H(9*A*)	65 (2)	79 (2)	202 (3)	2·9 (5)
H(9*B*)	154 (2)	128 (2)	73 (4)	4·0 (6)
H(9*C*)	54 (2)	181 (1)	162 (3)	2·5 (5)

Table 2. *Intramolecular bond distances* (Å) *and angles* (°)*, with e.s.d.'s in parentheses*

Atoms related by a twofold axis in the molecule are shown with a prime.

O(1)–C(4)	1·429 (3)	C(5)–C(6)	1·531 (3)
O(2)–C(6)	1·420 (3)	C(4)–C(7)	1·505 (3)
O(3)–C(4)	1·437 (2)	C(5)–C(8)	1·533 (3)
O(3)–C(6′)	1·418 (2)	C(5)–C(9)	1·529 (3)
C(4)–C(5)	1·540 (3)		

O(1)–C(4)–O(3)	109·8 (2)	C(4)–C(5)–C(6)	103·4 (2)
O(2)–C(6)–O(3′)	110·5 (2)	C(4)–C(5)–C(8)	111·9 (2)
O(1)–C(4)–C(5)	108·6 (2)	C(4)–C(5)–C(9)	112·5 (2)
O(1)–C(4)–C(7)	106·2 (2)	C(6)–C(5)–C(8)	110·0 (2)
O(3)–C(4)–C(5)	108·4 (2)	C(6)–C(5)–C(9)	109·5 (2)
O(3)–C(4)–C(7)	106·5 (2)	C(8)–C(5)–C(9)	109·4 (2)
O(2)–C(6)–C(5)	110·8 (2)	C(4)–O(1)–C(4′)	113·4 (2)
O(3′)–C(6)–C(5)	110·3 (2)	C(6)–O(2)–C(6′)	109·6 (2)
C(5)–C(4)–C(7)	117·2 (2)	C(4)–O(3)–C(6′)	111·6 (1)

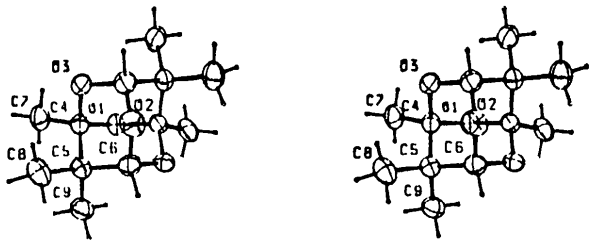


Fig. 1. A stereoview of the molecule and the numbering of the non-H atoms. Ellipsoids of 50% probability are used for non-H atoms; the H atoms are represented as spheres equivalent to $B = 0{\cdot}1$ Å^2.

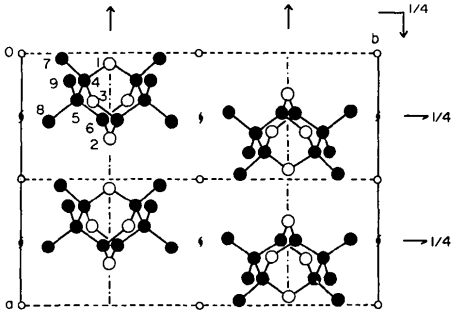


Fig. 2. Projection of the crystal structure along **c**. Filled circles denote C atoms and open circles O atoms. H atoms are omitted. The numbering of non-H atoms is shown for the asymmetric unit at x, y, z.

The twofold symmetry of the free molecule is preserved in the crystals. The twofold axis passes through O(1) and O(2). The molecules related by a c translation and by an n and thus a glide planes are packed into a hexagonal array to form a sheet parallel to (010). The sheet is stacked along **b** to complete the *Pbna* structure. All the interatomic contacts are normal van der Waals interactions.

It is interesting to note briefly the crystallographic pedigree (Haisa, 1978) of adamantanes. The room-temperature form of adamantane belongs to $Fm3m$ (Nordman & Schmitkons, 1965), and its low-temperature form to $P\bar{4}2_1c$ (Nordman & Schmitkons, 1965; Donohue & Goodman, 1967). Hexamethylenetetramine belongs to $I\bar{4}3m$ (Becka & Cruickshank, 1963), which is a subgroup of $Fm3m$ and supergroup of $P\bar{4}2_1c$, and *Pbna* of the present crystals is a subgroup of $P\bar{4}2_1c$. The hexamethylenetetramine–*m*-cresol complex belongs to *Ccc*2 (Mak, Yu & Lam, 1978), which is also a subgroup of $P\bar{4}2_1c$. The molecular symmetry is fully or partly preserved in all the crystals mentioned above.

The two symmetrically independent six-membered rings in the tetraoxaadamantane skeleton take a chair conformation; *i.e.* the plane through O(3), C(5), C(6) and C(6′) is planar within 0·013 (3) Å; C(4) deviates from the plane by −0·724 (3) Å, and O(2) by 0·673 (3) Å. The plane through O(1), C(4), C(6) and O(3′) is planar within 0·002 (3) Å; C(5) deviates by −0·784 (3) Å, and C(4′) by 0·637 (3) Å.

Absolute values of the endocyclic torsion angles are in the range 56·6 (2) to 62·6 (2)°. Some relevant exocyclic torsion angles characterizing the conformation of the side chains are: C(6)–C(5)–C(4)–C(7) −179·6 (2), O(1)–C(4)–C(5)–C(8) 178·4 (2), O(2)–C(6)–C(5)–C(9) −178·8 (2) and C(4)–C(5)–C(6)–H(6) −178 (1)°. These indicate that there is no significant distortion in the molecule. The fact that the compound is easily formed by the condensation of (2) is in accord with this strain-free conformation of the molecule.

The C–C and C–O bond lengths are normal, except for C(4)–C(7) which is slightly short. Such a shortening has been observed in other acetals (Chadwick & Dunitz, 1978), and seems to be caused by the electron-withdrawing effects of the O atoms attached to C(4). All the endo- and exocyclic bond angles except C(5)–C(4)–C(7) are close to an sp^3 angle. The widening of C(5)–C(4)–C(7) seems to be caused by the intramolecular repulsions: C(7)···H(9*A*) 2·99 (3), H(7*C*)···H(9*A*) 2·46 (4) Å. This is consistent with the observation in the ^{13}C NMR spectrum that the signal for C(7) appeared at higher field (20·5 – 21·1 p.p.m.) than is usual for the methyl C of cyclic acetals, 25·0 – 24·7 p.p.m. (Pearce, Gore & Silverstein, 1977), probably because of the steric effect (Dorman, Jautelat & Roberts, 1971).

The authors thank Professor Masao Kakudo, Dr Noritake Yasuoka and the staff of the Crystallographic Research Center, Institute for Protein Research, Osaka University, for use of the diffractometer.

References

ALMQVIST, S.-O. (1968). *Acta Chem. Scand.* **22**, 1367–1368.
ASHIDA, T. (1973). *The Universal Crystallographic Computing System – Osaka.* The Computation Center, Osaka Univ., Japan.
BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. R. Soc. London Ser. A*, **273**, 435–454.
CHADWICK, D. J. & DUNITZ, J. D. (1978). *Acta Cryst.* B**34**, 965–968.
DONOHUE, J. & GOODMAN, S. H. (1967). *Acta Cryst.* **22**, 352–354.
DORMAN, D. E., JAUTELAT, M. & ROBERTS, J. D. (1971). *J. Org. Chem.* **36**, 2757–2766.
FUJII, S. (1979). *The Universal Crystallographic Computing System – Osaka.* The Computation Center, Osaka Univ., Japan.
HAISA, M. (1978). *Acta Cryst.* A**34**, 753–759.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–73. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN* 78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MAK, T. C. W., YU, W.-H. & LAM, Y.-S. (1978). *Acta Cryst.* B**34**, 2061–2063.
NORDMAN, C. E. & SCHMITKONS, D. L. (1965). *Acta Cryst.* **18**, 764–767.
PEARCE, G. T., GORE, W. E. & SILVERSTEIN, R. M. (1977). *J. Magn. Reson.* **27**, 497–507.