

Fig. 2. Stereoscopic view of the packing in the cell viewed perpendicular to the *ab* plane. Methyl hydrogens are omitted for clarity.

out of the ring plane. The methyl groups of the neopentyl residue adopt a normal staggered conformation while the torsion angles down the C(13)–C(1) and C(13)–C(7) vectors between the C(14)–C(13) bond and the plane of the benzene ring are $+72.1$ and -70.8° respectively. These angles are equivalent to the angles $\tau_1[\text{C}(2)\text{--C}(1)\text{--C}(13)\text{--C}(14)]$ and $\tau_2[\text{C}(8)\text{--C}(7)\text{--C}(13)\text{--C}(14)]$ used by Hovmöller, Norrestam & Palm (1977) in their description of the conformational aspects of a number of DDT analogues and compare with the $+82$ and -66° , respectively, for the equivalent angles in GH44. Intramolecular distances and angles are normal. However, the *exo* C(1), C(7) and C(4), C(10) angles are distorted. Similar effects were found in GH44 and a number of other DDT analogues (Smith, 1978). The mode of packing of the molecules in the cell, van der Waals in nature, is

illustrated in Fig. 2 showing discrete molecular units with no significant intermolecular contacts [minimum, 3.36 (1) Å, O(10)···C(18)].

The authors wish to thank Dr Edward F. Rogers of Merck, Sharp & Dohme Research Laboratories, Rahway, New Jersey, for suggesting the problem and for providing a sample for the investigation. We also thank the Universities of Queensland and Stockholm for financial support and for the use of facilities, and the Queensland Institute of Technology for provision of data-preparation services. One of us (GS) thanks the Queensland Institute of Technology for leave to work on this project.

References

- CSIRO (1969). British Patent 1221380.
 DELACY, T. P. & KENNARD, C. H. L. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 2141–2147.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst. A* **24**, 390–397.
 HOLAN, G. (1969). *Nature (London)*, **221**, 1025–1029.
 HOVMÖLLER, S., NORRESTAM, R. & PALM, T.-B. (1977). *Acta Cryst. B* **33**, 377–381.
 HOVMÖLLER, S., SMITH, G. & KENNARD, C. H. L. (1978). *Cryst. Struct. Commun.* **7**, 589–593.
 ROGERS, E. F., BROWN, H. D., RASMUSSEN, I. M. & HEAL, R. E. (1953). *J. Am. Chem. Soc.* **75**, 2991–2999.
 SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SMITH, G. (1978). PhD thesis, Univ. of Queensland, Australia.
 SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1977). *Aust. J. Chem.* **29**, 743–747.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1980). **B36**, 1695–1698

Structure of *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane Dihydrate*

BY P. GLUZIŃSKI, J. W. KRAJEWSKI AND Z. URBAŃCZYK-LIPKOWSKA

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

(Received 2 December 1979; accepted 28 February 1980)

Abstract. $\text{C}_{16}\text{H}_{36}\text{N}_4 \cdot 2\text{H}_2\text{O}$, $M_r = 320.51$, tetragonal, $I4_1/a$ (origin at $\bar{1}$), $Z = 8$, $a = b = 18.647$ (4), $c = 12.021$ (3) Å, $V = 4179.8$ Å³, $d_m = 1.026$, $d_c = 1.029$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.465$ mm⁻¹. 2288

* For a preliminary communication see Krajewski, Urbańczyk-Lipkowska & Gluźniński (1979).

reflections were measured; of these only 870 independent reflections had $I > 2\sigma_I$. The structure was solved by direct methods and refined by the full-matrix least-squares method to a final $R = 0.091$ ($R_w = 0.051$, weights from counting statistics). The molecule appears to have C_i symmetry and a slightly deformed crown conformation with equatorial methyl

groups in positions 7 and 14. A rather complex hydrogen-bonding space system is present in the crystal.

Introduction. The title compound (Curtis, 1964) belongs to the family of fourteen-membered macrocyclic amines whose stereochemistry has been of interest for several years. The structure of the compounds has been discussed mainly in terms of their IR spectra (Stetter & Mayer, 1961; Curtis, 1964, 1968; Bosnich, Poon & Tobe, 1965; Jeżowska-Trzebiatowska, Koliński, Korybut-Daszkievicz, Mroziński & Wojciechowski, 1969; Dodziuk, Koliński & Korybut-Daszkievicz, 1973).

X-ray investigations of these compounds were rather few; the 7,14-dimethyl-5,12-diphenyl derivative was studied by Ferguson, Roberts, Lloyd & Hideg (1977), the diperchlorate of the unsubstituted amine (cyclam) by Nave & Truter (1974), the racemic monohydrate of the title compound by Krajewski, Urbańczyk-Lipkowska & Gluziński (1977), and recently, the racemic 7,12-dimethyl derivative of cyclam by Urbańczyk-Lipkowska, Krajewski, Gluziński, Andreotti & Bocelli (1980).

A colourless crystal 0.3 × 0.3 × 0.2 mm was chosen for diffractometric measurements and protected from the atmosphere. Space group *I*₄/*a* (centrosymmetric, origin at $\bar{1}$, No. 88) was determined from Weissenberg photographs by the systematically absent reflections (*hkl*: $h + k + l \neq 2n$; *hk0*: $h(k) \neq 2n$; *00l*: $l \neq 4n$; $a = b$) and was confirmed by the diffractometric collection of intensities without the fourfold-axis restriction. The measurements were made on a CAD-4 four-circle single-crystal diffractometer (SLAF & BS, Kraków) with Cu *K*α radiation using the $\omega/2\theta$ scan mode in the region up to $2\theta_{\max} = 150^\circ$. From 2288 collected intensities, 870 with $I > 2\sigma$, were considered as independently observed. These were used in further refinement cycles. The number of molecules in the unit cell ($Z = 8$) indicated that the molecule must be situated at a special position. The structure was solved by the direct method (program *SHELX*, Sheldrick, 1976); this revealed the approximate positions of all non-hydrogen atoms of the ring moiety and of three methyl substituents. The molecule was found to be centered at $(\frac{1}{2}, 1, \frac{1}{2})$. The remaining water O atom was found from a three-dimensional *F_o* Fourier synthesis. The refinement process was then performed by the least-squares full-matrix method (program *CRYLSQ*, XRAY 70 system, Stewart, Kundell & Baldwin, 1970) and involved four stages: (1) refinement with individual isotropic thermal parameters and unit weights, (2) refinement with anisotropic thermal parameters and weights from counting statistics ($1/\sigma_F^2$), (3) addition of geometrically calculated C-attached H-atom coordinates (program *XANADU*, Roberts & Sheldrick, 1975) as

Table 1. *Fractional atomic coordinates for the independent unit* ($\times 10^4$, for H atoms $\times 10^3$) with *e.s.d.*'s in parentheses

The symmetry operation for the second half of the molecule is $1 - x, 2 - y, 1 - z$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq.} (Å ²)*
N(1)	4093 (2)	10629 (2)	5420 (4)	4.1 (3)
C(2)	3547 (3)	10047 (3)	5277 (6)	5.0 (4)
C(3)	3658 (3)	9681 (3)	4172 (5)	4.8 (4)
N(4)	4345 (2)	9300 (2)	4176 (4)	3.8 (3)
C(5)	4553 (4)	9014 (4)	3070 (5)	4.6 (4)
C(6)	5259 (4)	8585 (3)	3254 (5)	4.9 (4)
C(7)	5949 (3)	9018 (3)	3479 (5)	4.9 (4)
C(8)	4005 (3)	8465 (3)	2608 (6)	7.4 (5)
C(9)	4670 (3)	9628 (3)	2238 (5)	6.2 (4)
C(10)	6604 (3)	8505 (3)	3469 (5)	7.4 (5)
O _w	5660 (2)	8361 (2)	6351 (4)	5.9 (2)
H(N1)	450 (2)	1037 (2)	539 (3)	
H(N4)	439 (2)	884 (2)	470 (4)	
H(O _w)1	575 (2)	869 (2)	571 (3)	
H(O _w)2	528 (3)	826 (2)	637 (4)	

* Calculated from refined anisotropic thermal parameters (deposited).

invariants and refining as in (2), (4) addition of N- and O_w-attached H-atom coordinates found from a difference Fourier synthesis, refining in an isotropic mode (damping factor 0.3), and finally refining all non-hydrogen parameters gave a shift/error value <0.05. The final reliability factors were $R = 0.091$ and $R_w = 0.051$. Table 1 gives the final refined atomic coordinates.*

Discussion. The bond lengths and bond angles found in the molecule are in Tables 2 and 3. Table 4 gives the torsion angles. A significant bond-length difference may be noticed for various C—N bonds. In the N—C—C—N ring segment the C—N bond lengths are markedly unequal: they differ by 0.033 (7) Å, the shorter bond involving the N atom lying closer to the C(5) atom with the geminal methyl groups. Conversely, the C—N bond lengths in the N—C—C—N ring segment are equal within their standard deviations; similarly for the bond angles at both N atoms (Table 3). It may be said generally that the C—N bond lengths observed (Table 2) are rather longer than in other secondary amines. The N—H bond lengths differ slightly, the shorter being found for the H atom involved in the internal hydrogen bond (Table 5). Both N atoms possess a pyramidal configuration. The water

* Lists of structure factors and anisotropic thermal parameters of the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35165 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

N(1)–C(2)	1.498 (7)	C(5)–C(8)	1.549 (9)
C(2)–C(3)	1.508 (9)	C(5)–C(9)	1.536 (9)
C(3)–N(4)	1.465 (7)	C(6)–C(7)	1.544 (9)
N(4)–C(5)	1.484 (8)	C(7)–N(1) ⁱ	1.480 (8)
C(5)–C(6)	1.556 (9)	C(7)–C(10)	1.552 (9)
N(1)–H(N1)	0.90 (4)	O _w –H(O _w)1	1.00 (4)
N(4)–H(N4)	1.06 (4)	O _w –H(O _w)2	0.74 (5)

Symmetry code: (i) 1 – x, 2 – y, 1 – z.

Table 3. Bond angles (°) with *e.s.d.*'s in parentheses

C(7) ⁱ –N(1)–C(2)	112.9 (5)	C(5)–C(6)–C(7)	117.4 (5)
N(1)–C(2)–C(3)	109.7 (5)	C(6)–C(7)–N(1) ⁱ	110.2 (5)
C(2)–C(3)–N(4)	109.6 (5)	C(6)–C(7)–C(10)	109.4 (5)
C(3)–N(4)–C(5)	113.6 (5)	N(1) ⁱ –C(7)–C(10)	108.8 (5)
N(4)–C(5)–C(6)	106.2 (5)	C(2)–N(1)–H(N1)	100 (2)
N(4)–C(5)–C(8)	112.7 (5)	C(7) ⁱ –N(1)–H(N1)	109 (2)
N(4)–C(5)–C(9)	110.7 (5)	C(3)–N(4)–H(N4)	118 (2)
C(6)–C(5)–C(8)	105.6 (5)	C(5)–N(4)–H(N4)	103 (2)
C(6)–C(5)–C(9)	110.9 (5)	H(O _w)1–O–H(O _w)2	110 (4)
C(8)–C(5)–C(9)	110.7 (5)		

Symmetry code: (i) 1 – x, 2 – y, 1 – z.

Table 4. Torsion angles (°) with *e.s.d.*'s in parentheses

C(7) ⁱ –N(1)–C(2)–C(3)	–176.0 (5)
N(1)–C(2)–C(3)–N(4)	66.3 (6)
C(2)–C(3)–N(4)–C(5)	–171.3 (5)
C(3)–N(4)–C(5)–C(6)	–175.9 (5)
N(4)–C(5)–C(6)–C(7)	–72.6 (6)
C(5)–C(6)–C(7)–N(1) ⁱ	68.5 (7)
C(6)–C(7)–N(1) ⁱ –C(2) ⁱ	–164.2 (5)
C(3)–N(4)–C(5)–C(8)	–60.8 (6)
C(3)–N(4)–C(5)–C(9)	63.7 (6)
C(8)–C(5)–C(6)–C(7)	167.6 (5)
C(9)–C(5)–C(6)–C(7)	47.7 (7)
C(5)–C(6)–C(7)–C(10)	–171.9 (5)
C(10)–C(7)–N(1) ⁱ –C(2) ⁱ	75.9 (6)

Symmetry code: (i) 1 – x, 2 – y, 1 – z.

Table 5. Possible hydrogen-bridge distances and angles in the crystal lattice

	D...A (Å)	D–H...A (Å)	∠D–H...A (°)
N(1)–H(N1)...N(4) ⁱ	2.956 (6)	2.31 (4)	129 (3)
N(4)–H(N4)...O ⁱⁱ	3.208 (6)	2.21 (4)	156 (3)
O _w –H(O _w)1...N(1) ⁱ	2.879 (6)	1.88 (4)	175 (4)
O _w –H(O _w)2...O ⁱⁱⁱ	2.872 (5)	2.15 (5)	166 (5)

Symmetry code: (i) 1 – x, 2 – y, 1 – z; (ii) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$.

molecule is distinguished by the strong inequality of its O–H bond lengths: 1.00 (4) and 0.74 (5) Å. Also, the H–O–H bond angle is rather unusual: 110 (4)°. This may be due to the involvement of these H atoms in different types of intermolecular hydrogen bridges in the crystal lattice (Table 5).

Analysis of Table 4 leads to the conclusion that the fourteen-membered ring of this cyclam derivative approximates to a crown conformation; this may be seen from the *ORTEP* diagram (Fig. 1, Johnson, 1965). This feature is rather unusual for fourteen-membered macrocycles which are believed to belong to the diamond-type conformation (Dunitz & Ibers, 1968). The same may be observed for cyclam diperchlorate (Nave & Truter, 1974) and the 7,14-dimethyl-5,12-diphenyl derivative (Ferguson *et al.*, 1977). The other two reported cyclam-derivative conformations (Krajewski *et al.*, 1977; Urbańczyk-Lipkowska *et al.*, 1980) have exact or approximate twofold-axis symmetry for the ring and, therefore, cannot be compared directly with the present case. Nevertheless, they are not of the diamond type.

The deviation from the ideal crown conformation of the cyclam derivative reported here involves not only various bond lengths and angles of particular ring members, but also a slight ring twist. This ring distortion may be shown by calculation of the dihedral angle between the central plane formed by C(2), C(3), C(2)ⁱ and C(3)ⁱ, and the least-squares plane defined by N(4), C(5), C(7) and N(1)ⁱ (Fig. 1). This angle was found to be 5.6°.

A very similar ring twist may be found when one calculates the analogous dihedral angle for cyclam derivatives reported by Nave & Truter (1974) or Ferguson *et al.* (1977). For the former case the angle was calculated to be 4.7°; for the second, the deviation of the molecule from *C_i* symmetry requires that two

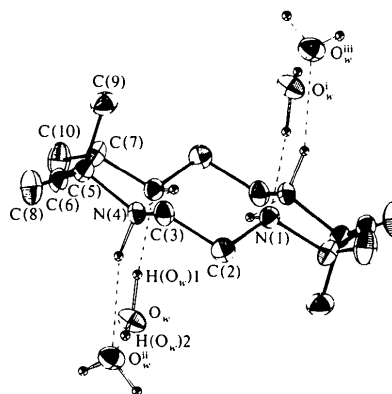


Fig. 1. Parallel projection of the molecule. The N,N,N,N plane is bent by 10° to the viewer. Thermal-motion ellipsoids of the non-hydrogen atoms are set at the 40% probability level. The hydrogen-bonding system shown involves water molecules generated by the symmetry operations (i) 1 – x, 2 – y, 1 – z; (ii) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$; (iii) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z$. H atoms attached to C atoms are not shown.

different angles be calculated: 1·2 and 2·2°. In order to elucidate whether the observed ring twist is due to steric effects in the ring itself, the free cyclam amine (in the absence of water molecules) has been modelled (including all H atoms and lone electron pairs at N atoms) by the strain-energy-minimization method (program MM1, Allinger, Sprague & Yuh, 1975). It appears that the minimized strain energy for the amine molecule possessing C_{2h} symmetry may be reduced by about 5% when the symmetry of the molecule at the start of the minimization is reduced to C_i (by deleting the plane and axis restrictions). A ring twist of 3·34° is then observed as a result of ring-geometry optimization. Despite the fact that such a modelling attempt gives only a crude approximation to the truth (e.g. the internal hydrogen-bonding effect was not taken into account), it may be said that the observed ring twist in cyclam derivatives may be partly due to internal steric effects.

The authors are much indebted to Dr R. A. Koliński for supplying the compound samples and for valuable discussions. The courtesy of the Head Manager Mr A. Pleniewicz, Dr J. Szymczyk and Dr A. Koczyk of the Research and Development Center of Industrial Projecting 'BISTYP', Warszawa, enabled the authors to prepare the ORTEP diagram.

References

ALLINGER, N. L., SPRAGUE, J. T. & YUH, Y. H. (1975). Molecular mechanics programs MM1 and MMP1. Univ. of Georgia, USA.

- BOSNICH, B., POON, C. K. & TOBE, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.
- CURTIS, N. F. (1964). *J. Chem. Soc.* pp. 2644–2650.
- CURTIS, N. F. (1968). *Coord. Chem. Rev.* **3**, 3–47.
- DODZIUK, H., KOLIŃSKI, R. A. & KORYBUT-DASZKIEWICZ, B. (1973). *Spectrochim. Acta Part A*, **29**, 511–521.
- DUNITZ, J. D. & IBERS, J. A. (1968). *Perspect. Struct. Chem.* **2**, 18–21.
- FERGUSON, G., ROBERTS, P., LLOYD, D. & HIDE, K. (1977). *J. Chem. Soc. Chem. Commun.* pp. 149–150.
- JEŻOWSKA-TRZEBIATOWSKA, B., KOLIŃSKI, R. A., KORYBUT-DASZKIEWICZ, B., MROZIŃSKI, J. & WOJCIECHOWSKI, W. (1969). *Bull. Acad. Pol. Sci. Sér. Sci. Chim.* **17**, 411–418.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KRAJEWSKI, J. W., URBAŃCZYK-LIPKOWSKA, Z. & GLUZIŃSKI, P. (1977). *Cryst. Struct. Commun.* **6**, 817–822.
- KRAJEWSKI, J. W., URBAŃCZYK-LIPKOWSKA, Z. & GLUZIŃSKI, P. (1979). Vth European Crystallographic Meeting, Copenhagen, p. 127.
- NAVE, C. & TRUTER, M. R. (1974). *J. Chem. Soc. Dalton Trans.* pp. 2351–2354.
- ROBERTS, P. & SHELDRIK, G. M. (1975). XANADU. Program for crystallographic calculations. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). SHELX. Program for crystal structure determination. Univ. of Cambridge, England.
- STETTER, H. & MAYER, K.-H. (1961). *Chem. Ber.* **94**, 1410–1416.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- URBAŃCZYK-LIPKOWSKA, Z., KRAJEWSKI, J. W., GLUZIŃSKI, P., ANDRETTI, G. D. & BOCELLI, G. (1980). In preparation.

Acta Cryst. (1980). **B36**, 1698–1700

Ohchinolide A, a New Limonoid from *Melia azedarach* L. var. *japonica* Makino

BY HIROSHI NAKAI AND MOTOO SHIRO

Shionogi Research Laboratory, Shionogi & Co. Ltd, Fukushima-ku, Osaka 553, Japan

AND MASAMITSU OCHI

Faculty of Science, Kochi University, Asakura, Kochi 780, Japan

(Received 25 December 1979; accepted 25 February 1980)

Abstract. C₃₇H₄₂O₁₀, monoclinic, P2₁, *a* = 16·284 (1), *b* = 9·648 (1), *c* = 10·700 (1) Å, β = 98·08 (1)°, *Z* = 2, *D_x* = 1·29, *D_m* = 1·30 Mg m⁻³. The structure was solved by the direct method and refined by the block-diagonal least-squares technique to *R* = 0·049 for 2949 reflexions. Rings *A* and *B* are in the chair

conformation, ring *C* is in the boat conformation, and rings *D* and *E* take the envelope form.

Introduction. The molecular structures of ohchinolide A and B, isolated from an ether extract of the dry fruit of *Melia azedarach* L. var. *japonica* Makino, have been