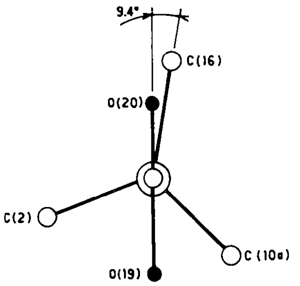

Fig. 5. Projection de Newman suivant les atomes C(15)—C(1) (pour l'angle de torsion, $\sigma = 0{,}9°$).

celles généralement rencontrées pour de telles conformations. Dans le cas du cycloheptane, les distances interatomiques sont en accord avec les valeurs admises pour des liaisons $C(sp^3)$—$C(sp^3)$. Il faut noter la faible valeur de l'angle C(8)—C(12)—C(11) = 91,9 (3)° provoquée par un encombrement stérique important.

Quelques distances intramoléculaires très courtes sont présentées sur la Fig. 4. Sur la Fig. 3, le cycle encombré a été décomposé en cinq cycles afin de faciliter la notation des valeurs des angles dièdres.

Sur la projection de Newman suivant les atomes C(15)—C(1) (Fig. 5) les atomes d'oxygène O(19) et O(20) sont en position éclipsée par rapport au méthyl C(16). L'angle entre les plans O(20)—C(15)—C(1) et C(15)—C(1)—C(16) est en effet égal à 9,4°. En milieu cristallin, il n'existe aucune liaison hydrogène et la distance intermoléculaire (C—C) la plus faible sépare les atomes de carbone C(9) et (C14): C(9)—C(14) = 3,62 (1) Å.

L'analyse radiocristallographique a permis de définir la structure de cette molécule obtenue par isomérisation de l'époxy-7,8α isopimarate de méthyle. En raison de la nature de son squelette, dérivé du benz[*a*]azulène on peut envisager l'utilisation de ce composé pour la synthèse de molécules biologiquement actives.

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Structure of (±)-5,12-Dimethyl-1,4,8,11-tetraazacyclotetradecane

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Abstract. $C_{12}H_{28}N_4$, $M_r = 228{\cdot}37$, m.p. = 382–383 K, orthorhombic, *Fddd*, $a = 16{\cdot}884$ (3), $b = 34{\cdot}637$ (9), $c = 9{\cdot}809$ (2) Å, $V = 5736{\cdot}4$ Å^3, $Z = 16$, $d_m = 1{\cdot}05$ Mg m^{-3} (by flotation), $F(000) = 2048$, μ(Cu $K\alpha$) = 0·435 mm^{-1}. The structure was solved by direct methods and refined by a full-matrix least-squares method to $R = 0{\cdot}048$ and $R_w = 0{\cdot}035$ for 950 observed reflections. Two pairs of unsymmetrical bifurcated hydrogen bonds forming six- and five-membered chelate rings are found in the fourteen-membered tetramine ring.

Introduction. The X-ray analysis of 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (DMC) was undertaken as part of a systematic structural study of a range of 1,4,8,11-tetraazacyclotetradecane (cyclam) derivatives which are potential ligands in transition-metal complexes (*cf.* Krajewski, Urbańczyk-Lipkowska & Gluziński, 1977; Gluziński, Krajewski & Urbańczyk-Lipkowska, 1980). The compound has been obtained by Koliński & Korybut-Daszkiewicz (1969). The infrared spectra of the compound were discussed

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(Dodziuk, Koliński & Korybut-Daszkiewicz, 1973) and some suggestions concerning the conformation of the ring and possible internal hydrogen bonding have been made on the basis of these spectra. The verification of these proposals by X-ray structural methods seems to be of particular interest.

The X-ray intensities were measured from a monocrystal sealed in a Lindemann-glass capillary tube. 1801 reflections were collected on a Siemens single-crystal four-circle diffractometer in the range up to $\theta_{max} = 60°$ using the $\omega/2\theta$ scan technique and Ni-filtered Cu $K\alpha$ radiation. 950 independent reflections with $I > 2\sigma_I$ were selected and used for structure determination and refinement. A standard reflection measured after every 25 reflections gave no indication of crystal decay.

The structure was solved by direct methods (*SHELX*, Sheldrick, 1976) in the orthorhombic space group *Fddd* (No. 70, origin at $\bar{1}$). The number of molecules in the unit cell ($Z = 16$) indicated that they must be situated on crystallographic symmetry elements (centres or twofold axes). The best set of phases gave an E map which clearly displayed all non-H atoms of the molecule on the twofold axis $\frac{1}{8},y,\frac{1}{8}$. Thus, the compound must be racemic.

The refinement of non-H atomic parameters was performed by the full-matrix least-squares method (program *CRYLSQ* in XRAY 70, Stewart, Kundell & Baldwin, 1970) in the isotropic and then the anisotropic mode. Positional parameters of all H atoms were obtained from a difference Fourier map. They were added to the atom set with individual isotropic temperature factors equal to $B_{eq} + 1$ of their associate atoms. Six cycles of refinement (H atom temperature factors held invariant) resulted in final R and R_w values of 0·048 and 0·035, respectively (weights from statistics). Table 1 gives the refined fractional coordinates of all atoms in the asymmetric unit.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z	B^*_{eq} (Å^2)
N(1)	147 (1)	5291 (0)	1918 (2)	4·14 (8)
C(2)	236 (1)	5241 (1)	3387 (2)	4·71 (11)
C(3)	868 (1)	5503 (1)	3957 (2)	4·48 (10)
N(4)	1638 (1)	5430 (0)	3338 (1)	3·80 (8)
C(5)	2151 (1)	5770 (1)	3300 (2)	3·98 (10)
C(6)	2894 (1)	5689 (1)	2469 (2)	4·65 (11)
C(7)	2767 (1)	5645 (1)	946 (2)	5·06 (12)
C(8)	2361 (1)	5891 (1)	4754 (2)	5·46 (14)
H(N1)	−114 (9)	5090 (4)	1598 (16)	
H1(C2)	469 (10)	4963 (4)	3528 (17)	
H2(C2)	−320 (10)	5271 (5)	3867 (17)	
H1(C3)	713 (9)	5799 (4)	3838 (17)	
H2(C3)	916 (10)	5451 (4)	4977 (18)	
H(N4)	1552 (9)	5346 (4)	2528 (15)	
H(C5)	1819 (10)	6026 (4)	2820 (16)	
H1(C6)	3150 (9)	5447 (4)	2851 (16)	
H2(C6)	3289 (10)	5933 (5)	2654 (16)	
H1(C7)	2444 (12)	5882 (5)	599 (19)	
H2(C7)	3306 (11)	5683 (5)	406 (18)	
H1(C8)	1802 (11)	5999 (5)	5366 (18)	
H2(C8)	2668 (11)	5711 (5)	5186 (18)	
H3(C8)	2745 (10)	6118 (5)	4649 (17)	

* Calculated from anisotropic thermal parameters by $B_{eq} = 8\pi^2(U_1U_2U_3)^{1/3}$.

Discussion. Based on investigations of the energetically favourable conformations for various macrocycles, the diamond conformation was predicted by Dunitz & Ibers (1968) for fourteen-membered rings. The prediction was supported later by strain-energy calculations (Dale, 1973), and verified by the crystal structure determinations of cyclotetradecanone (Groth, 1975) and cyclotetradecane (Groth, 1976) which both possess diamond conformations. The X-ray examination of tetraoxacyclotetradecane (Bassi, Scordamaglia & Fiore, 1972) and the two forms of tetrathiacyclotetradecane (De Simone & Glick, 1976) revealed that replacement of four C atoms by four O or S atoms does not alter the fourteen-membered ring conformation significantly.

The crystal structures of 1,8-diazacyclotetradecane dibromide (Dunitz & Meyer, 1965) and 1,8-dihydroxy-1,8-diazacyclotetradecane (Brown, 1966) also revealed diamond conformations of the ring. However, if four C atoms are replaced by imino groups, fundamental conformational changes in the ring may be observed. Nave & Truter (1974) have found that 1,4,8,11-tetraazacyclotetradecane (cyclam) diperchlorate exists in an approximate crown conformation. This observation was confirmed later for *meso*-5,12-dimethyl-7,14-diphenylcyclam (Ferguson, Roberts, Lloyd & Hideg, 1977) and *meso*-5,5,7,12,12,14-hexamethylcyclam dihydrate (HMC-2Hy) (Gluziński *et al.*,

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

N(1)–C(2)	1·459 (3)	N(4)–C(5)	1·461 (2)
N(1)–C(7)^{i}	1·456 (3)	C(5)–C(6)	1·522 (3)
C(2)–C(3)	1·508 (3)	C(5)–C(8)	1·528 (3)
C(3)–N(4)	1·457 (3)	C(6)–C(7)	1·517 (3)
N(1)–H(N1)	0·882 (15)	C(6)–H1(C6)	1·016 (15)
C(2)–H1(C2)	1·050 (17)	C(6)–H2(C6)	1·091 (17)
C(2)–H2(C2)	1·055 (17)	C(7)–H1(C7)	1·044 (18)
C(3)–H1(C3)	1·065 (16)	C(7)–H2(C7)	1·061 (18)
C(3)–H2(C3)	1·020 (17)	C(8)–H1(C8)	1·179 (19)
N(4)–H(N4)	0·860 (15)	C(8)–H2(C8)	0·917 (18)
C(5)–H1(C5)	1·150 (15)	C(8)–H3(C8)	1·023 (17)

(i) Atom generated by the symmetry operation $\frac{1}{4} - x, y, \frac{1}{4} - z$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35693 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(2)–N(1)–C(7)^{i}	113·0 (2)	N(4)–C(5)–C(8)	109·6 (2)
N(1)–C(2)–C(3)	111·6 (2)	C(6)–C(5)–C(8)	111·0 (2)
C(2)–C(3)–N(4)	111·9 (2)	C(5)–C(6)–C(7)	115·4 (2)
C(3)–N(4)–C(5)	113·6 (1)	N(1)^{i}–C(7)–C(6)	113·2 (2)
N(4)–C(5)–C(6)	110·8 (2)		
H(N1)–N(1)–C(2)	108 (1)	H1(C6)–C(6)–C(5)	108 (1)
H(N1)–N(1)–C(7)^{i}	110 (1)	H1(C6)–C(6)–C(7)	110 (1)
H1(C2)–C(2)–N(1)	106 (1)	H2(C6)–C(6)–C(5)	106 (1)
H1(C2)–C(2)–C(3)	104 (1)	H2(C6)–C(6)–C(7)	109 (1)
H2(C2)–C(2)–N(1)	110 (1)	H1(C6)–C(6)–H2(C6)	109 (1)
H2(C2)–C(2)–C(3)	114 (1)	H1(C7)–C(7)–N(1)^{i}	109 (1)
H1(C2)–C(2)–H2(C2)	111 (1)	H1(C7)–C(7)–C(6)	108 (1)
H1(C3)–C(3)–C(2)	112 (1)	H2(C7)–C(7)–N(1)^{i}	113 (1)
H1(C3)–C(3)–N(4)	110 (1)	H2(C7)–C(7)–C(6)	111 (1)
H2(C3)–C(3)–C(2)	108 (1)	H1(C7)–C(7)–H2(C7)	101 (1)
H2(C3)–C(3)–N(4)	108 (1)	H1(C8)–C(8)–H2(C8)	116 (1)
H1(C3)–C(3)–H2(C3)	107 (1)	H1(C8)–C(8)–H3(C8)	109 (1)
H(N4)–N(4)–C(3)	107 (1)	H1(C8)–C(8)–C(5)	112 (1)
H(N4)–N(4)–C(5)	111 (1)	H2(C8)–C(8)–H3(C8)	102 (2)
H1(C5)–C(5)–N(4)	110 (1)	H2(C8)–C(8)–C(5)	112 (1)
H1(C5)–C(5)–C(6)	109 (1)	H3(C8)–C(8)–C(5)	105 (1)
H1(C5)–C(5)–C(8)	106 (1)		

(i) Atoms generated by the symmetry operation $\frac{1}{4}-x, y, \frac{1}{4}-z$.

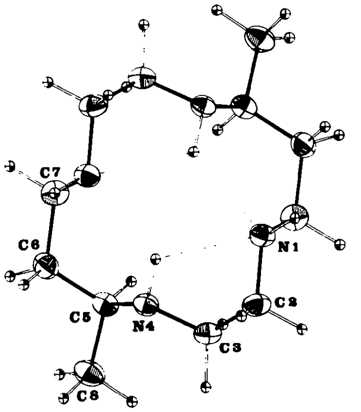

Fig. 1. *ORTEP* projection of the molecule down the *b* axis. Thermal-motion ellipsoids are at the 40% probability level. H atoms are shown as spheres of arbitrary radius.

1980). Another ring shape has been found for (±)-5,5,7,12,12,14-hexamethylcyclam monohydrate (HMC-1Hy) (Krajewski *et al.*, 1977), where the cyclam ring presents approximate (space group $C2/c$, molecule found in general position) C_2 point-group symmetry, the twofold axis being perpendicular to the ring mean plane.

The present case may compare well with the last-mentioned compound. Tables 2 and 3 give the bond lengths and valence angles found in the DMC molecule. Fig. 1 presents an *ORTEP* (Johnson, 1965) projection of the molecule down the *b* axis.

Examination of the bond lengths and angles does not reveal any peculiarities. Because the molecule of DMC has crystallographic C_2 symmetry, the detailed ring-conformation differences between DMC and HMC-1Hy are analysed by considering the torsion angles in the two molecules (Table 4).

The torsion angles of the ring may be divided into two groups according to their absolute values indicating the mutual configuration of the 1,4 atoms involved: *anti* position (*a*) (angle > 150°) and *gauche* position (*g*) (< 75°). According to this, the following configuration sequence of bonds [starting from N(1) through N(1)^{i} (i = symmetry operation $\frac{1}{4}-x, y, \frac{1}{4}-z$)] may be established for both macro rings: (–*g*–*g*–*a*–*a*–*g*–*g*–*a*–) (×2) for DMC and (–*a*–*g*–*a*–*a*–*g*–*g*–*g*–)(×2) for HMC-1Hy. The two sequences differ from each other by the configuration order in the C(7)^{i}–N(1)–C(2) fragment of the ring. This superposition apparently causes the nearly C_2-symmetric trimethylene ring fragments in HMC-1Hy to be significantly twisted in opposite directions, in contrast to those of the DMC molecule. The tetrahedron which may be formed by four N atoms of the ring is in fact much more flat in DMC than in HMC-1Hy. The distance between the tetrahedral edges N(1)···N(1)^{i} and N(4)···N(4)^{i} is 0·48 Å in DMC, whereas in HMC-1Hy the equivalent distance is 1·32 Å (average).

Consideration of the torsion angles involving the methyl group at C(5) [atom C(8)] clearly shows its equatorial position with respect to the N(4)–C(5)–C(6) ring fragment. Sterically, the methyl groups in DMC are equivalent to the lone methyl groups in HMC-1Hy.

Like all other investigated cyclam derivatives, the DMC molecular structure reveals the possibility of weak unsymmetric bifurcated hydrogen bonds. The H atom attached to N(4) is directed towards the interior of the ring giving potential hydrogen-bonding distances H(N4)···N(1) = 2·454 (16) and H(N4)···N(1)^{i} = 2·347 Å. The angles at H(N4) are found to be N(4)–H(N4)···N(1) = 114·5° and N(4)–H(N4)···N(1)^{i} = 133° (Fig. 1).

The possibility of the existence of four internal hydrogen bonds inside the fourteen-membered heteroring may be regarded as the real cause of the non-diamond conformations of cyclam derivatives. In fact, examination of the internal interatomic distances of the N–H···N type in all hypothetically possible cyclam rings of diamond-like (rectangular) conformation reveals that there is no possibility of closing a six- or five-membered chelate ring without violating the rectangular ring shape.

The only interatomic distance shorter than 2·5 Å involving one H and one non-H atom is found in the DMC crystal between H(N1) and N(4) at $-\frac{1}{4}+x, 1-y, -\frac{1}{4}+z$. Its H···N length is found to be 2·324 (15) Å and the angle at the H atom is 175·5°. This allows us to suggest the possible existence of a weak intermolecular hydrogen bridge forming infinite chains of molecules in the crystal lattice.

The details of the molecular packing and the

Table 4. *Torsion angles (°) in DMC and HMC-1Hy with e.s.d.'s in parentheses*

DMC		Inverted molecule of HMC-1Hy*			
Angles in the ring					
C(7)^{i}–N(1)–C(2)–C(3)	−75·2 (2)	C(10)–N(1)–C(1)–C(2)	177·9 (3)	C(5)–N(3)–C(6)–C(7)	177·9 (3)
N(1)–C(2)–C(3)–N(4)	−59·6 (2)	N(1)–C(1)–C(2)–N(2)	−64·5 (4)	N(3)–C(6)–C(7)–N(4)	−62·2 (4)
C(2)–C(3)–N(4)–C(5)	151·2 (2)	C(1)–C(2)–N(2)–C(3)	172·6 (3)	C(6)–C(7)–N(4)–C(8)	169·1 (3)
C(3)–N(4)–C(5)–C(6)	−171·2 (2)	C(2)–N(2)–C(3)–C(4)	−162·7 (3)	C(7)–N(4)–C(8)–C(9)	−164·6 (3)
N(4)–C(5)–C(6)–C(7)	69·8 (2)	N(2)–C(3)–C(4)–C(5)	65·9 (4)	N(4)–C(8)–C(9)–C(10)	69·0 (4)
C(5)–C(6)–C(7)–N(1)^{i}	−70·3 (2)	C(3)–C(4)–C(5)–N(3)	−68·8 (5)	C(8)–C(9)–C(10)–N(1)	−69·1 (4)
C(6)–C(7)–N(1)^{i}–C(2)^{i}	−177·4 (2)	C(4)–C(5)–N(3)–C(6)	−74·8 (4)	C(9)–C(10)–N(1)–C(1)	−74·3 (4)
Angles involving equatorial methyl groups					
(*a*) The lone methyl groups					
C(7)–C(6)–C(5)–C(8)	−168·2 (2)	C(5)–C(4)–C(3)–C(13)	−173·0 (3)	C(10)–C(9)–C(8)–C(16)	−169·6 (3)
C(3)–N(4)–C(5)–C(8)	65·1 (2)	C(2)–N(2)–C(3)–C(13)	76·7 (4)	C(7)–N(4)–C(8)–C(16)	73·9 (4)
(*b*) From geminal methyl pairs					
		C(8)–C(9)–C(10)–C(12)	167·8 (3)	C(3)–C(4)–C(5)–C(15)	168·5 (3)
		C(1)–N(1)–C(10)–C(12)	45·9 (5)	C(6)–N(3)–C(5)–C(15)	45·3 (4)
Involving axial methyl groups (from geminal pairs)					
		C(8)–C(9)–C(10)–C(11)	48·1 (4)	C(3)–C(4)–C(5)–C(14)	49·0 (4)
		C(1)–N(1)–C(10)–C(11)	164·8 (3)	C(6)–N(3)–C(5)–C(14)	164·4 (3)

(i) Atoms generated by the symmetry operation $\frac{1}{2} - x, y, \frac{1}{2} - z$.

* Krajewski *et al.* (1977). The angle definitions use the atom numbers conforming to those of the reference cited.

potential hydrogen-bonding lattice in the crystal structure of DMC will be discussed, along with other cyclam derivatives, in a separate paper.

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