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## The Crystal and Molecular Structure of (2*R*,5*R*,8*R*,11*R*)-2,5,8,11-Tetraethyl-1,4,7,10-tetraazacyclododecane

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$C_{16}N_4H_{36}$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.392(2)$ ,  $b = 9.422(2)$ ,  $c = 43.162(10)$  Å,  $U = 3819(2)$  Å<sup>3</sup>,  $D_m = 1.00$ ,  $D_c = 0.99$  g cm<sup>-3</sup>,  $Z = 8$ . The structure is pseudo tetragonal, and was solved by a trial and error method. The azacyclododecane ring forms a square conformation, typical of the 12-membered cycloalkanes.

## Introduction

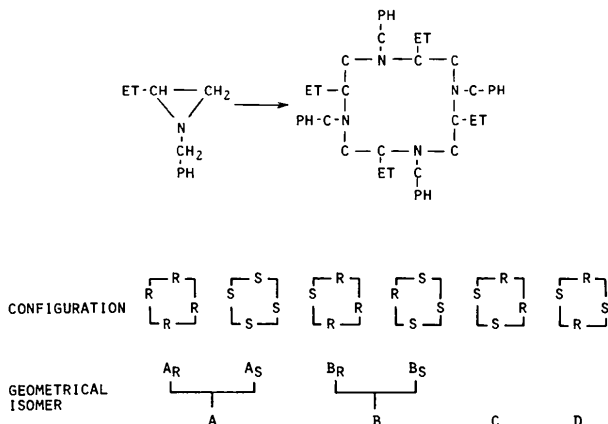
Several cyclic tetramers of chiral aziridines have been synthesized in our Institute (Tsuboyama, Tsuboyama, Higashi & Yanagita, 1970). These tetramers have four different geometrical isomers depending on the chirality of the original aziridine, as shown in Fig. 1.

Corresponding to these geometrical differences, many crystal forms were obtained, and the lattice parameters and the space groups were reported

(Tsuboyama, Tsuboyama, Uzawa & Higashi, 1974). Also, some derivatives of these tetramers form interesting clathrate-type compounds with several aromatic molecules. However, none of the structures has yet been solved. Therefore, in order to establish the fundamental geometry of these tetramers using a simple form of this series, the title compound was synthesized and the X-ray diffraction study was performed.

## Experimental

Single crystals were obtained by recrystallization from benzene–acetonitrile solution. The crystal consists of transparent square plates which pile up to form a square pyramid. For the X-ray diffraction work, a plate was stripped off from the pile and cut to a narrow plate with dimensions 0.5 × 0.2 × 0.1 mm. X-ray diffraction data were measured on a Rigaku automated four-circle diffractometer with graphite-monochromatized Cu  $K\alpha$  radiation. Within the range of  $2\theta \leq 140^\circ$ , 998 independent reflections were observed. The crystal at first appeared to be tetragonal  $P4_12_12$  (or  $P4_32_12$ ) with  $a = 9.4$  and  $c = 43.2$  Å. However, careful examination of the lattice parameters and the intensity distribution revealed that the crystal belongs to the orthorhombic system  $P2_12_12_1$ .



### Structure determination

The crystal contains two independent molecules in the asymmetric unit. Since the structure is pseudo tetragonal with one molecule in the asymmetric unit, the structure was first solved for the tetragonal cell.

#### (a) Determination of the pseudo tetragonal structure

The structure was solved by a trial and error method with a molecular model built by the computer (Sakurai & Kobayashi, 1972). From a NMR study of this compound (Tsuboyama, Tsuboyama, Uzawa, Kobayashi & Sakurai, 1977), the ring was estimated to have a square conformation, similar to the cyclododecane ring (Dunitz & Shearer, 1960). Based on this square conformation, various molecular models are still possible, depending on the positions and angles of the ethyl group. For these models, the intramolecular van der Waals energy was calculated and the model shown in Fig. 2(a) was selected as having a reasonably low energy value. Thus, with 143 reflections with  $\sin \theta/\lambda \leq 0.22$ , an  $R$ -index map was calculated (Sakurai, Ito & Kobayashi, 1968) within the Cheshire group (Hirshfeld, 1968) of  $P4_12_12$ , *i.e.*  $P4_22$ . Since the

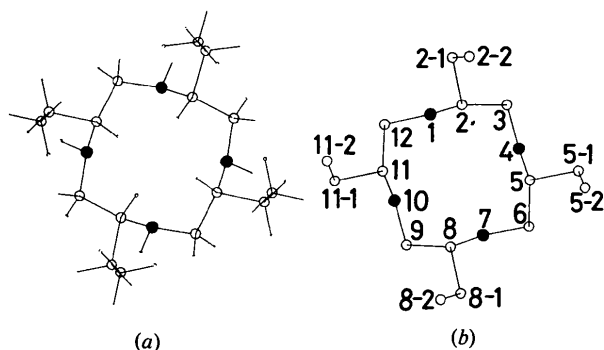


Fig. 2. Molecular shape. (a) The initial model. The nitrogen atom is denoted by the black circle. (b) The structure in the pseudo tetragonal cell.

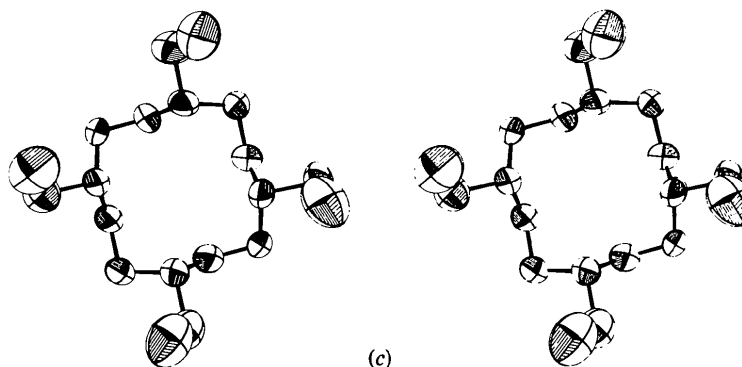


Fig. 2 (cont.). (c) A stereodrawing of molecule I.

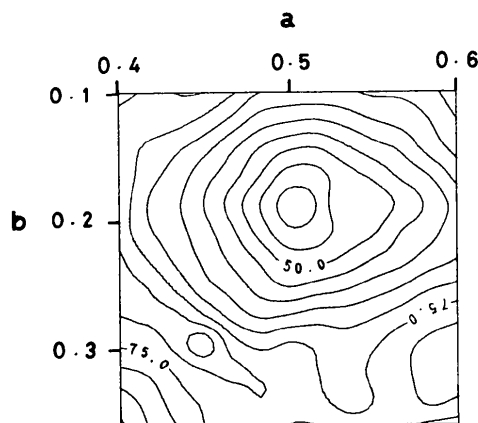


Fig. 3. A section of the  $R$  index map, parallel to the original  $ab$  plane. The rotation angle is  $55^\circ$ , and the  $z$  coordinate is 0.09. Contour lines are plotted for every 5% of the  $R$  index.

molecular model has a fourfold axis, it was assumed that the symmetry axis is along the tetragonal  $c$  axis. Therefore, the trial parameters were the rotation about the  $c$  axis and three translations along the cell edges. The rotation range was between 0 and  $90^\circ$ .

The  $R$ -index map shows a sharp minimum at the rotation angle  $55^\circ$  and  $z = 0.09$ . A section of the map near the minimum is shown in Fig. 3. Starting from this position,  $R$  index 38%, the structure was refined by the block-diagonal least-squares method and the  $R$  index converged to 25%. The structure obtained at this stage (Fig. 2b) is essentially the same as the original model, with the exception of the direction of the terminal methyl group.

#### (b) Determination of the true structure

The structure obtained for the pseudo tetragonal cell is the mean structure of the two independent molecules in the orthorhombic cell. The true space group  $P2_12_12_1$  is a subgroup of  $P4_12_12$ , and is obtained from the latter by removing the  $4_1$  operation. Therefore, the second molecule in the asymmetric unit of the orthorhombic

cell can be generated from the mean molecule by the 4<sub>1</sub> operation. Considering the difference of the origin in these two space groups (*International Tables for X-ray Crystallography*, 1965), two molecules in the asymmetric unit, molecule I and molecule II, were generated from the mean molecular coordinates  $x_m$ ,  $y_m$  and  $z_m$  of the tetragonal cell by the operations,

$$\begin{cases} x_1 = -\frac{1}{4} + x_m \\ y_1 = y_m \\ z_1 = \frac{1}{8} + z_m \end{cases} \quad \text{and} \quad \begin{cases} x_{11} = \frac{1}{4} - y_m \\ y_{11} = \frac{1}{2} + x_m \\ z_{11} = \frac{3}{8} + z_m \end{cases}$$

Table 1. Comparison of the three models

The numbering of the sites in the ring is given in Fig. 5. The refinement was performed with anisotropic temperature factors; the mean value,  $B$  ( $\text{\AA}^2$ ), of the equivalent temperature factor of each site is listed.

Atom site	Model 1 (correct)		Model 2 (nitrogen at the corner)		Model 3 (all carbon)	
	Species of atom	$B$	Species of atom	$B$	Species of atom	$B$
1	N	6.3	C	4.0	C	4.4
2	C	7.2	C	6.5	C	7.0
3	C	6.3	N	10.3	C	8.0
Bond length ( $\text{\AA}$ ) between						
1-2		1.52		1.50		1.49
2-3		1.54		1.55		1.56
3-1'		1.51		1.50		1.50
$R$ index (%)		10.8		12.8		11.2

Then the structure was refined by successive block-diagonal least-squares methods. The temperature factors of the terminal ethyl groups became very large, as shown in the *ORTEP* drawing (Fig. 2c) (Johnson, 1965). In spite of these large temperature factors, when all methyl C atoms were omitted and the difference Fourier synthesis was performed, all methyl C atoms were recovered at the same places. However, because of the large temperature factors, H atoms were not located satisfactorily by the difference synthesis, and were not used for the calculation. The final  $R$  index was 10.8% with anisotropic temperature factors. In order to verify that the N atoms were correctly assigned, two additional model structures were calculated. The second model put the N atoms at the corner of a square, and the third assumed all atoms to be C. Both models were refined by least squares, and the results are compared in Table 1. The final  $R$  indices were 12.8 and 11.2% for the second and third models respectively. In the original structure (first model), the temperature factors are similar for all sites in the ring. In the other models, that for site 1 is always smaller than the others. Therefore, the atom at site 1 must be heavier than the others. The distance between sites 2 and 3 is always equal to the normal C-C bond length, while those between 1 and 2, and 3 and 1 are slightly shorter. These facts clearly indicate that the N atoms are correctly located in the original structure.

Table 2. Atomic parameters

Positional parameters are multiplied by  $10^4$ . The equivalent temperature factors ( $\text{\AA}^2$ ) are given in the last column. The numbering scheme of the atoms is shown in Fig. 2(b).

	Molecule I				Molecule II			
	$x$	$y$	$z$	$B_{eq}$	$x$	$y$	$z$	$B_{eq}$
N(1)	5690 (12)	9088 (12)	7717 (3)	6.8	1403 (12)	3173 (12)	9783 (3)	6.3
N(4)	8741 (12)	9788 (12)	7702 (3)	6.5	2058 (12)	6170 (11)	9781 (3)	6.2
N(7)	9366 (12)	6797 (11)	7748 (3)	6.2	-1014 (11)	6851 (11)	9766 (3)	5.8
N(10)	6320 (12)	6096 (11)	7749 (3)	6.3	-1649 (11)	3855 (11)	9752 (3)	6.0
C(2)	6368 (15)	10006 (15)	7970 (3)	6.2	2261 (16)	3803 (15)	9522 (4)	6.4
C(3)	7596 (15)	10781 (14)	7805 (4)	7.4	3106 (15)	5085 (15)	9657 (4)	7.3
C(5)	9612 (15)	9213 (15)	7973 (4)	6.3	1414 (16)	7047 (15)	9523 (4)	6.7
C(6)	10444 (16)	7909 (15)	7857 (4)	7.1	143 (15)	7844 (15)	9668 (4)	6.9
C(8)	8695 (16)	5958 (14)	8014 (4)	6.3	-1819 (15)	6222 (15)	9490 (4)	6.4
C(9)	7461 (15)	5156 (15)	7871 (4)	7.1	-2656 (16)	4943 (15)	9623 (4)	7.1
C(11)	5443 (15)	6749 (15)	8009 (4)	6.2	-952 (15)	2970 (14)	9505 (3)	5.8
C(12)	4629 (15)	8012 (15)	7854 (4)	7.5	256 (15)	2190 (15)	9670 (4)	7.2
C(2)1	5231 (19)	11150 (18)	8080 (4)	8.9	3428 (19)	2653 (19)	9421 (4)	8.9
C(2)2	5668 (26)	11576 (23)	8393 (4)	12.8	3858 (23)	2979 (24)	9098 (5)	12.1
C(5)1	10761 (20)	10385 (19)	8070 (4)	9.2	2549 (19)	8170 (18)	9412 (4)	9.2
C(5)2	11258 (23)	10132 (27)	8392 (4)	12.7	2194 (25)	8684 (22)	9100 (4)	12.3
C(8)1	9830 (19)	4915 (18)	8163 (4)	9.1	-2923 (18)	7403 (16)	9377 (4)	8.2
C(8)2	9392 (24)	4456 (25)	8478 (5)	12.8	-3345 (25)	7078 (23)	9047 (5)	12.4
C(11)1	4322 (18)	5632 (18)	8121 (4)	8.6	-2089 (20)	1826 (17)	9383 (4)	8.8
C(11)2	3745 (22)	6113 (23)	8432 (4)	11.0	-1544 (23)	1269 (21)	9070 (4)	11.0

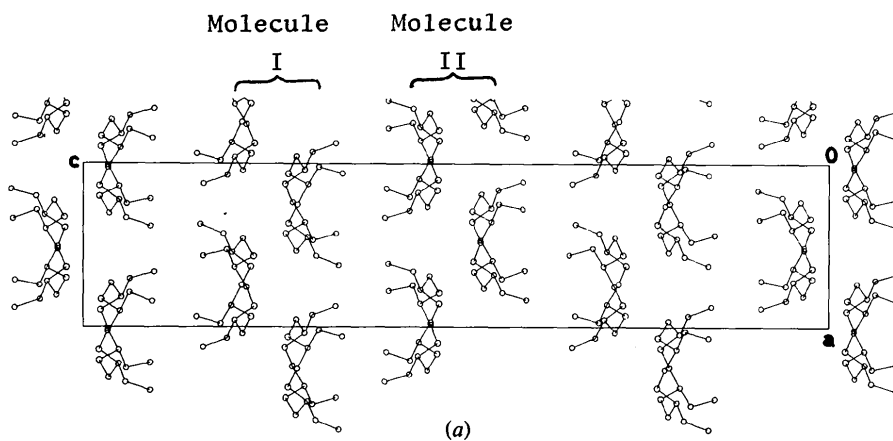
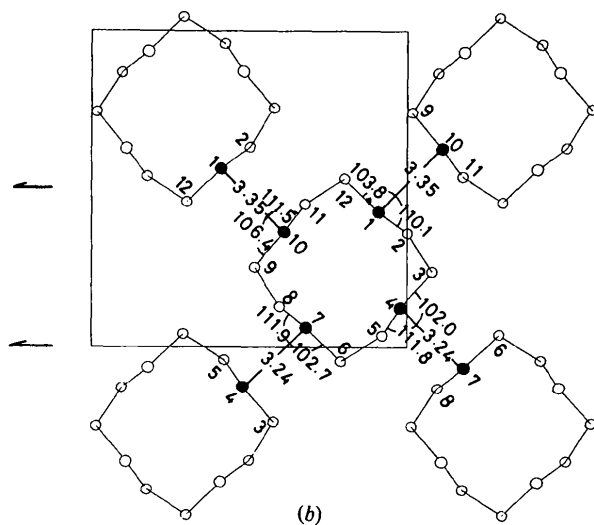
Fig. 4. Crystal structure. (a) Projection along *b*.

Fig. 4 (cont.). (b) Packing of the azacyclododecane ring.

The atomic parameters are given in Table 2.\* A stereodrawing of the molecule is shown in Fig. 2(c).

### Discussion of the structure

The crystal consists of layer arrays of molecules, parallel to the *ab* plane (Fig. 4). Each layer consists of two molecules related by a crystallographic  $2_1$

\* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33105 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

operation parallel to *a* or *b*. The azacyclododecane ring is almost parallel to the *ab* plane and the main short intermolecular distances are between the N atoms related by the  $2_1$  operation, as shown in Fig. 4(b). Because of the bulky ring arrangement, the ethyl groups occupy a lot of space. The cross-section per ethyl chain is almost 20% larger than that of the close-packed hydrocarbon chain in normal paraffins. This is the reason why the ethyl group has such large temperature factors. So much extra space creates the possibility of forming various clathrate-type compounds in some derivatives of this series.

The geometries of the two independent molecules are essentially the same. Although the standard deviation of each bond length, *ca* 0.02 Å, is large because of the relatively large *R* index, the molecule has approximate  $C_4$  symmetry. Therefore, instead of the individual bond lengths and angles, the geometry of the average molecule with  $C_4$  symmetry is given in Table 3 and Fig. 5. The square conformation in the present structure is similar to that of the following related 12-membered rings: cyclododecane (Dunitz & Shearer, 1960), azacyclododecane (Dunitz & Weber, 1964), tetraoxacyclododecane (Anet, Krane, Dale, Daasvatn & Kristiansen, 1973). When compared with cyclododecane, the last column of Table 3, asymmetry of the torsion angles at the two sides of the corner atom is observed. This average structure will be used as the fundamental geometry in the further study of this series of compounds.

The calculations were performed on a FACOM 230-75 computer at this Institute, with the UNICS II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). The research was supported, in part, by a Scientific Grant (134041) from the Ministry of Education.

Table 3. Average structure with  $C_4$  symmetry

Coordinates are given in Å with respect to the three principal axes.

Site	Molecule I			Molecule II			Cyclododecane
	X	Y	Z	X	Y	Z	
1 (N)	1.89	0.81	-1.26	0.40	2.02	-1.24	
2 (C)	2.23	-0.15	-0.12	1.38	1.75	-0.12	
3 (C corner)	2.20	-1.56	-0.75	2.52	0.92	-0.74	
2-1 (C ethyl)	3.70	0.15	0.38	1.97	3.15	0.36	
2-2 (C ethyl)	3.87	-0.42	1.74	2.53	2.97	1.74	
Torsion angles							
1-2-3-1'		-62.6°			-63.6°		-69.°
2-3-1'-2'		-75.5			-74.5		-69.
3-1'-2'-3'		166.1			166.0		158.

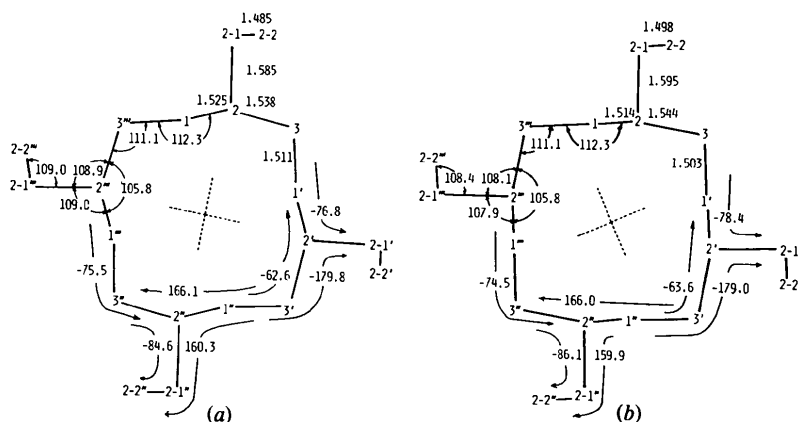


Fig. 5. Bond lengths, bond angles and torsion angles in the averaged structure with  $C_4$  symmetry. The torsion angles are defined by four consecutive atoms along the long arrow. The dotted lines at the center of the molecule are along the principal axes of the moment of inertia. (a) Molecule I. (b) Molecule II.

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