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Structure of (2*RS*,5*RS*,8*RS*,11*SR*)-1,4,7,10-Tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane

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Abstract. $C_{44}H_{60}N_4$, triclinic, $P\bar{1}$, $a = 11{\cdot}56\,(1)$, $b = 18{\cdot}60\,(2)$, $c = 9{\cdot}754\,(5)$ Å, $\alpha = 105{\cdot}10\,(6)$, $\beta = 106{\cdot}68\,(4)$, $\gamma = 85{\cdot}00\,(5)°$, $U = 1939{\cdot}0\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}10$, $D_c = 1{\cdot}104\,(1)$ Mg m^{-3}. The crystal structure was solved by the Monte Carlo direct method. The 12-membered ring has a distorted square conformation with the methylene groups at the corners.

Introduction. This paper is part of a series of investigations on the cyclic tetramers of chiral aziridines. These tetramers can be divided into four geometrical isomers, *viz* C_4, C_1, S_4 and C_i (Tsuboyama, Tsuboyama, Uzawa & Higashi, 1974). Among these, the crystal structures of C_4 (*RRRR*-type) (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978*a*,*b*), and C_i (*RRSS*-type) (Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979) have been reported. In this paper the structure of the title compound with C_1 symmetry (*RRRS*-type) is described. Triclinic single crystals of the racemic compound (*RRRS* and *SSSR*) were obtained from ethyl acetate solution. A clear colourless plate crystal with dimensions 0·4 × 0·4 × 0·2 mm was used for the study. X-ray diffraction data were measured on a Rigaku AFC four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. Within the range $2\theta \leq 50°$, 4583 independent reflections with $|F| > 3\sigma(F)$ were obtained. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.

The first attempt to solve the structure by *MULTAN* (Main, Woolfson & Germain, 1971) was not successful. The Monte Carlo method (Furusaki, 1979) was then applied using 24 initial sets, and a reasonable solution was obtained through the *FASTAN* part of *MULTAN*.

The structure was refined by the block-diagonal least-squares method. Unit weight was given to all reflections, and anisotropic temperature factors were used for all non-hydrogen atoms. All H atoms were located by a difference Fourier synthesis, and included in the final refinement with isotropic temperature factors. The final *R* index was 5·4%. Atomic parameters are given in Table 1.*

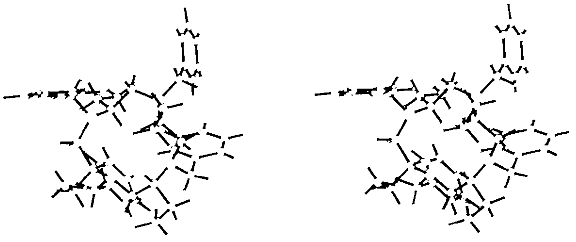

Fig. 1. Stereoscopic drawing of the molecule projected along the normal to the 12-membered ring.

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* Lists of structure factors and anisotropic temperature factors and a stereodiagram (with the 12-membered ring viewed from the side) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35281 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters*

Positional parameters are multiplied by 10^4 for C, N, and O atoms and by 10^3 for H atoms. The equivalent temperature factors (Å^2) are given in the last column. The numbering scheme of the atoms is the same as that of previous papers (Sakurai *et al.*, 1978*b*; Hiramatsu *et al.*, 1979) (*cf.* Fig. 2).

	x	y	z	B_{eq}
N(1)	5073 (2)	1691 (1)	6161 (3)	3·4
N(4)	4339 (2)	1577 (1)	2725 (3)	3·9
N(7)	4503 (3)	3267 (1)	3171 (3)	4·2
N(10)	4422 (2)	3548 (1)	6620 (3)	3·7
C(2)	3872 (3)	1696 (2)	5099 (4)	3·7
C(3)	3904 (3)	1177 (2)	3598 (4)	4·0
C(5)	3389 (3)	2052 (2)	2028 (4)	4·3
C(6)	3944 (4)	2711 (2)	1812 (4)	4·9
C(8)	3618 (3)	3654 (2)	3963 (4)	4·2
C(9)	4233 (3)	4032 (2)	5592 (4)	4·2
C(11)	5494 (3)	3046 (2)	6643 (4)	3·6
C(12)	5356 (3)	2394 (2)	7275 (3)	3·6
C(2)1	2818 (3)	1514 (2)	5624 (4)	5·0
C(2)2	1610 (4)	1784 (3)	4791 (6)	7·5
C(5)1	2522 (4)	1643 (2)	546 (4)	5·8
C(5)2	1317 (4)	2057 (3)	177 (6)	8·7
C(8)1	2785 (4)	4223 (2)	3237 (5)	6·5
C(8)2	1611 (4)	4343 (3)	3675 (7)	9·6
C(11)1	6698 (3)	3439 (2)	7486 (4)	4·4
C(11)2	7785 (3)	2956 (2)	7243 (5)	6·0
C(1)1	5260 (3)	1065 (2)	6852 (4)	4·1
C(1)2	6564 (3)	902 (2)	7484 (4)	4·0
C(1)7	7356 (4)	753 (2)	6622 (4)	5·4
C(1)6	8542 (4)	573 (3)	7180 (5)	6·7
C(1)5	8990 (4)	540 (3)	8635 (5)	6·6
C(1)4	8218 (4)	688 (3)	9507 (5)	6·8
C(1)3	7027 (4)	867 (2)	8947 (4)	5·6
C(4)1	4936 (3)	1068 (2)	1707 (4)	4·6
C(4)2	6239 (3)	914 (2)	2436 (3)	4·0
C(4)3	6710 (3)	196 (2)	2238 (4)	4·6
C(4)4	7929 (4)	62 (2)	2819 (4)	5·2
C(4)5	8687 (3)	649 (2)	3609 (4)	5·2
C(4)6	8224 (3)	1365 (2)	3828 (4)	5·2
C(4)7	7013 (3)	1500 (2)	3261 (4)	4·6
C(7)1	5202 (4)	3793 (2)	2812 (4)	5·2
C(7)2	6443 (4)	3515 (2)	2744 (4)	4·9
C(7)3	6685 (4)	3096 (2)	1433 (4)	6·1
C(7)4	7839 (4)	2852 (3)	1397 (5)	7·1
C(7)5	8785 (4)	3029 (3)	2652 (6)	7·6
C(7)6	8570 (4)	3450 (3)	3951 (5)	7·6
C(7)7	7413 (4)	3683 (2)	3989 (4)	6·2
C(10)1	4402 (3)	4009 (2)	8098 (4)	4·3
C(10)2	3127 (3)	4177 (2)	8219 (4)	4·3
C(10)3	2734 (4)	4892 (2)	8673 (5)	6·1
C(10)4	1575 (4)	5035 (3)	8829 (6)	8·2
C(10)5	814 (4)	4453 (3)	8541 (5)	7·5
C(10)6	1191 (4)	3739 (3)	8069 (6)	7·7
C(10)7	2339 (4)	3602 (2)	7915 (6)	6·7

	x	y	z	B
H(C2)	372 (2)	227 (1)	501 (3)	3·4 (0·6)
H(C3)1	302 (3)	91 (2)	298 (3)	4·5 (0·7)
H(C3)2	446 (3)	68 (2)	374 (3)	4·6 (0·7)
H(C5)	281 (3)	228 (2)	274 (3)	4·3 (0·7)
H(C6)1	465 (3)	251 (2)	136 (4)	5·8 (0·9)
H(C6)2	321 (3)	295 (2)	107 (4)	5·6 (0·8)
H(C8)	302 (3)	324 (2)	397 (3)	4·0 (0·7)
H(C9)1	369 (3)	450 (2)	595 (3)	4·9 (0·8)
H(C9)2	505 (3)	433 (2)	573 (3)	4·9 (0·8)
H(C11)	550 (3)	281 (2)	554 (3)	4·8 (0·8)
H(C12)1	467 (3)	254 (2)	782 (3)	3·8 (0·7)
H(C12)2	618 (2)	228 (1)	800 (3)	3·4 (0·6)
H(C2–1)1	278 (3)	92 (2)	547 (3)	4·9 (0·8)
H(C2–1)2	299 (3)	179 (2)	669 (4)	5·7 (0·8)
H(C2–2)1	133 (4)	144 (2)	364 (5)	9·7 (1·2)
H(C2–2)2	158 (4)	239 (2)	496 (5)	9·8 (1·2)
H(C2–2)3	96 (4)	167 (2)	524 (5)	9·2 (1·2)
H(C5–1)1	230 (3)	106 (2)	55 (4)	6·8 (0·9)
H(C5–1)2	287 (3)	156 (2)	−26 (4)	8·1 (1·1)
H(C5–2)1	69 (4)	176 (2)	−77 (5)	9·8 (1·2)
H(C5–2)2	146 (5)	268 (3)	27 (6)	13·7 (1·7)
H(C5–2)3	80 (5)	198 (3)	93 (6)	15·4 (1·8)
H(C8–1)1	323 (3)	475 (2)	359 (4)	6·7 (0·9)
H(C8–1)2	251 (4)	398 (2)	213 (5)	9·4 (1·2)
H(C8–2)1	114 (4)	473 (2)	332 (5)	11·1 (1·3)
H(C8–2)2	109 (5)	378 (3)	319 (6)	13·9 (1·7)
H(C8–2)3	166 (5)	456 (3)	471 (6)	14·1 (1·7)
H(C111)1	672 (3)	396 (2)	725 (4)	6·0 (0·9)
H(C111)2	682 (3)	364 (2)	860 (4)	5·6 (0·8)
H(C112)1	787 (3)	242 (2)	757 (4)	8·1 (1·1)
H(C112)2	855 (4)	324 (2)	787 (4)	8·7 (1·1)
H(C112)3	777 (4)	277 (2)	623 (4)	9·0 (1·2)
H(C1–1)1	482 (3)	55 (2)	599 (3)	4·8 (0·7)
H(C1–1)2	477 (3)	114 (2)	756 (4)	6·0 (0·9)
H(C1–7)	707 (4)	78 (2)	569 (4)	8·2 (1·1)
H(C1–6)	919 (4)	53 (2)	664 (4)	8·5 (1·1)
H(C1–5)	993 (3)	44 (2)	903 (4)	7·9 (1·1)
H(C1–4)	862 (4)	71 (3)	1063 (5)	12·3 (1·5)
H(C1–3)	648 (3)	99 (2)	956 (4)	7·6 (1·0)
H(C4–1)1	446 (3)	55 (2)	112 (3)	5·3 (0·8)
H(C4–1)2	497 (3)	133 (2)	95 (4)	6·6 (0·9)
H(C4–3)	615 (3)	−20 (2)	162 (3)	4·4 (0·7)
H(C4–4)	827 (3)	−50 (2)	266 (4)	7·3 (1·0)
H(C4–5)	965 (3)	58 (2)	411 (4)	7·1 (1·0)
H(C4–6)	878 (3)	180 (2)	448 (4)	7·0 (1·0)
H(C4–7)	667 (3)	203 (2)	344 (3)	4·8 (0·8)
H(C7–1)1	532 (3)	434 (2)	360 (4)	6·4 (0·9)
H(C7–1)2	470 (3)	394 (2)	191 (4)	6·8 (0·9)
H(C7–3)	595 (3)	292 (2)	56 (4)	7·7 (1·1)
H(C7–4)	800 (4)	243 (3)	40 (5)	11·8 (1·5)
H(C7–5)	969 (4)	286 (3)	266 (5)	10·9 (1·4)
H(C7–6)	936 (4)	366 (2)	495 (5)	10·3 (1·3)
H(C7–7)	732 (3)	408 (2)	495 (4)	7·4 (1·0)
H(C101)1	487 (3)	454 (2)	840 (3)	4·5 (0·7)
H(C101)2	483 (3)	371 (2)	880 (4)	6·2 (0·9)
H(C10–3)	332 (3)	532 (2)	886 (4)	7·5 (1·0)
H(C10–4)	125 (4)	561 (2)	912 (5)	9·7 (1·2)
H(C10–5)	−6 (3)	451 (2)	859 (4)	8·2 (1·1)
H(C10–6)	62 (4)	333 (2)	790 (5)	10·4 (1·3)
H(C10–7)	261 (4)	307 (2)	760 (4)	8·5 (1·1)

Discussion. A stereoscopic drawing of the *RRRS* molecule is shown in Fig. 1. The 12-membered ring forms a distorted square ring with the methylene groups at the corners. The torsion angles, bond lengths and angles in the ring are shown in Fig. 2. As seen in Fig. 1, the benzyl group and the neighbouring ethyl group extend in opposite directions from the 12-membered ring. Also, those which belong to the *R* carbon and the *S* carbon sides extend in opposite directions. Compared with the other types of related molecules (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978*a*,*b*; Hiramatsu *et al.*, 1979), some of

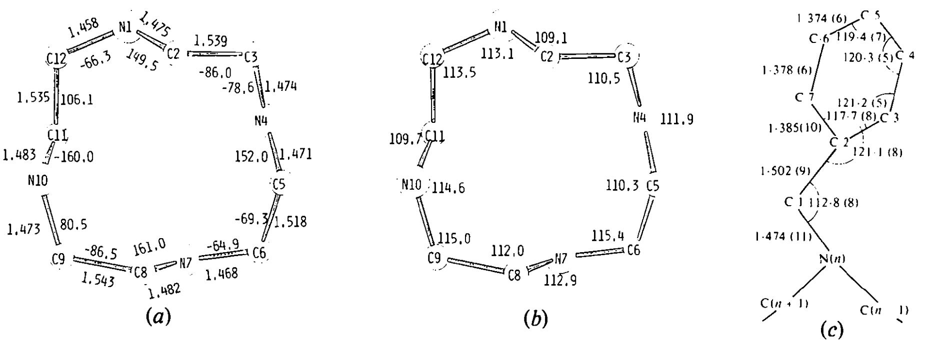

Fig. 2. The bond parameters. (*a*) Bond lengths (Å) and torsion angles (°) in the 12-membered ring. The torsion angles are given by the values inside the ring. The standard deviations are 0·004 Å for N—C, 0·005 Å for C—C, and 0·3° for the torsion angles. (*b*) Bond angles (°) in the 12-membered ring. The standard deviation is 0·3°. (*c*) Bond lengths (Å) and angles (°) in the benzyl groups. These are the mean values for the four independent groups.

Table 2. *Torsion angles (°) and bond angles (°) near the benzyl group*

	$n = 1$	$n = 4$	$n = 7$	$n = 10$
C(n − 1)–N(n)–C(n)1–C(n)2	−72·0 (3)	−83·2 (3)	−83·4 (4)	82·0 (3)
C(n + 1)–N(n)–C(n)1–C(n)2	159·6 (3)	148·6 (3)	150·6 (3)	−148·9 (3)
N(n)–C(n)1–C(n)2–C(n)3	125·9 (4)	133·5 (3)	90·4 (5)	−126·4 (4)
N(n)–C(n)1–C(n)2–C(n)7	−56·4 (5)	−50·2 (4)	−91·3 (5)	55·7 (5)
C(n − 1)–N(n)–C(n)1	110·8 (3)	111·3 (3)	109·0 (3)	109·3 (2)
C(n + 1)–N(n)–C(n)1	113·3 (3)	114·5 (3)	112·4 (3)	113·4 (2)

the torsion angles are less favourable, but the basic conformation can be described by the same principle. That is, the torsion angles along the side of the ring are |*g*|, |*t*|, |*g*| and the signs depend on the chirality of the carbon atom; −*g*, *t*, −*g* for the *R* side and *g*, −*t*, *g* for the *S* side. Despite the irregularity of the 12-membered ring, the bond lengths and angles of the benzyl groups are not significantly different. Average values are therefore shown in Fig. 2(*c*).

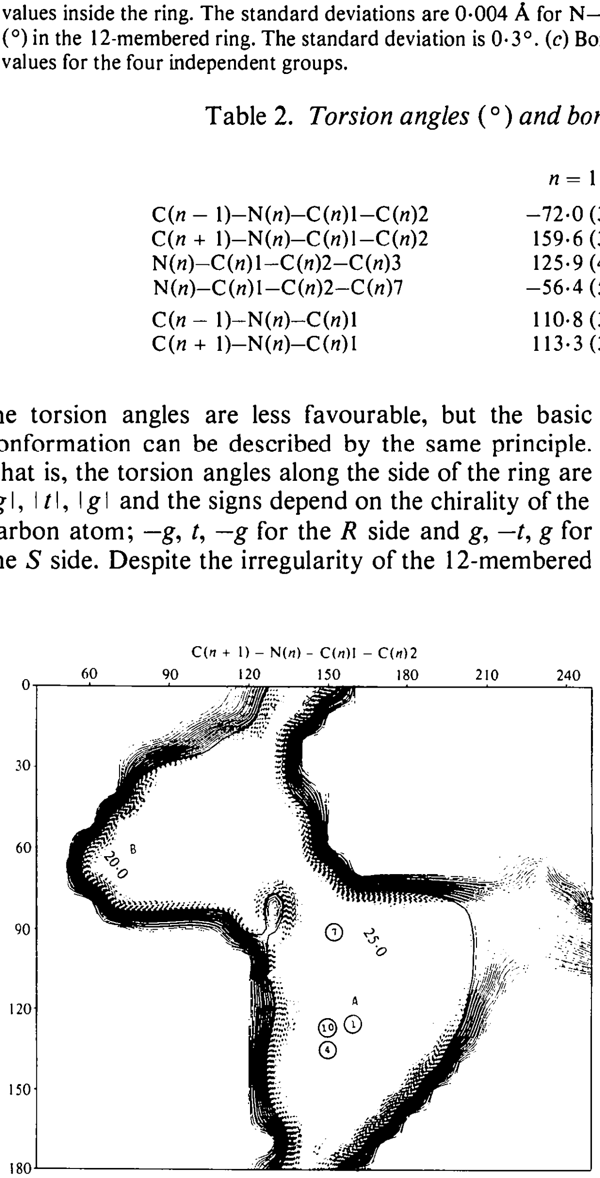

Fig. 3. The conformation-energy map for the *RRRS* molecule. The contour lines are drawn at intervals of 1 kcal mol^{-1} (1 kcal mol^{-1} ≡ 4·2 kJ mol^{-1}). The observed values are circled. For the 10-substituent (*S* side), the signs of the torsion angles are the opposite of those shown.

The conformation energy for the benzyl group has been calculated with respect to the rotation about the two single bonds in the benzyl group (Fig. 3). Throughout the calculation, the torsion angles about the four groups were changed simultaneously. For the group belonging to the *S* side, the torsion angles have opposite signs from the others. The resultant energy map shows the broad low-energy region *A*. The related observed values are shown in Table 2. The observed torsion angles are all within this broad minimum *A*. The second minimum *B* appears near the *g*, *g* position. But this region is narrow, and the energy is about 20 kJ mol^{-1} higher than that of region *A*. Therefore, the observed conformation will be maintained in solution.

Calculations were performed on a Facom 230-75 computer of this Institute using the *UNICS* III program system (Sakurai & Kobayashi, 1979) for the crystallographic and *MMB* 80 (Sakurai, 1978) for the conformation-energy calculations.

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Pyridoxamine Monohydrochloride†

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Abstract. $C_8H_{13}N_2O_2^+.Cl^-$, M_r = 204·7, monoclinic, space group *P*2/*c*, *a* = 7·893 (1), *b* = 9·057 (1), *c* = 13·507 (1) Å, β = 96·95 (2)°, *Z* = 4, D_c = 1·418 Mg m^{-3}, *R* = 0·058 for 1515 reflections with $|F_o| \geq 3\sigma(F_o)$. The pyridoxamine cations HPM$^+$ have a deprotonated phenolic group and protonated ring and amino N atoms. The cations are linked to the Cl$^-$ anions by an extensive hydrogen-bonding network.

Introduction. The crystal structure of pyridoxamine hydrochloride, HPM$^+$Cl$^-$, has been determined as part of our research on the structures and spectra of vitamin B$_6$ derivatives (K. J. Franklin & Richardson, 1978, 1980; T. A. Franklin & Richardson, 1980; Thompson, Balenovich, Hornich & Richardson, 1980). The infrared spectrum of HPMCl suggested that the stable tautomer of HPM$^+$ was one in which the phenolic group was ionized and the pyridine ring and amino group were protonated (T. A. Franklin & Richardson, 1980). This has been confirmed by the present crystal structure determination.

The crystals were prepared by evaporation of an aqueous equimolar solution of PM.2HCl and NaOH. Weissenberg photographs showed the absence of 0*k*0 reflections for *k* odd and *h*0*l* reflections for *l* odd, uniquely establishing the space group as *P*2/*c*. A single crystal was aligned about the *a** axis on a manual Picker diffractometer, and cell dimensions were determined with Zr-filtered Mo $K\alpha_1$ radiation (λ = 0·70926 Å). Data were collected by ω–2θ scans over a 2θ range of 2° at a rate of 1° min^{-1}. 10 s backgrounds were counted at each end of the scan range. A standard reflection was measured after every 25–50 reflections, and did not vary significantly during the data collection. The reflection intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. No absorption correction was made (μ = 0·372 mm^{-1}).

An *E* map revealed the non-hydrogen atoms, whose positions were refined by full-matrix least squares using the *SHELX* set of programs (Sheldrick, 1976). Scattering factors for neutral C, H, N, O, and Cl atoms were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, F_o and F_c are the observed and calculated structure factors, $w = [\sigma^2(F_o) + 0{\cdot}001\, F_o^2]^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. All non-hydrogen atoms were given anisotropic temperature factors. Positional parameters were refined for the five H atoms whose positions were not fixed geometrically [H(1),H(7), H(8),H(9),H(12)]. The H(2), H(3), and H(4) atoms were refined as part of a rigid methyl group. The positions of the other H atoms were calculated with $r_{\text{C-H}}$ = 1·08 Å. All H atoms were assigned isotropic thermal parameters *U* of 0·04 Å^2.

A total of 1700 reflections with $2\theta \leq 50°$ were measured of which 1515 had $|F_o| \geq 3\sigma(F_o)$ and were classified as observed. The weighted residual, $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$, was 0·063. There were no significant features on the final difference map.

The atomic positional parameters are presented in Table 1, and the numbering scheme is shown in Fig. 1.§

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† 4-Aminomethyl-3-hydroxy-5-hydroxymethyl-2-methylpyridine hydrochloride.

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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 35328 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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