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

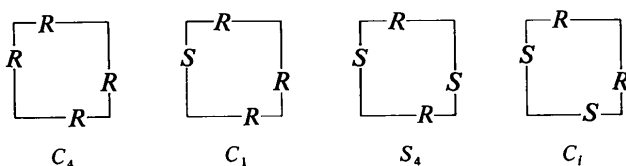
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Abstract. $C_{44}H_{60}N_4$, monoclinic, $P2_1/c$, $a = 9.345$ (4), $b = 9.327$ (4), $c = 22.358$ (11) Å, $\beta = 94.14$ (8)°, $U = 1944$ (2) Å³, $D_m = 1.11$, $D_c = 1.10$ Mg m⁻³, $Z = 2$. The 12-membered ring forms an armchair conformation with the methylene groups at the top and the toe.

Introduction. This paper forms part of a series of investigations on the cyclic tetramers of chiral aziridines. These tetramers can be divided into four geometrical isomers as shown below (Tsuboyama, Tsuboyama, Uzawa & Higashi, 1974).



Recently, the two crystal structures with C_4 symmetry, *i.e.* (2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane (TETA) (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978*a*), and (2*RS*,5*RS*,8*RS*,11*RS*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane (*RRRR*-type) (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978*b*) were reported. In this paper the structure of the title compound with C_i symmetry (*RRSS*-type) is described.

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Triclinic single crystals were obtained from benzene solution (Tsuboyama *et al.*, 1974). However, many of these crystals were twinned or disordered and were not suitable for the structural work. Therefore they were recrystallized from dioxane solution, and a different crystal form was obtained. The new crystals belong to the monoclinic system $P2_1/c$ with $Z = 2$, and possess intramolecular centrosymmetry. The size of the crystal used was 0.4 × 0.4 × 0.45 mm. X-ray diffraction data were measured on a Rigaku automated AFC four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Within the range $2\theta \leq 50^\circ$, 2132 independent reflections were observed. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.

The structure was solved by the direct phasing method, and all H atoms were deduced from successive difference Fourier syntheses. 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. The final R index was 4.8%. Atomic parameters are given in Table 1.†

Discussion. A stereoscopic drawing of the molecule is shown in Fig. 1. When projected on the mean plane of

† Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34202 (14 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 10⁴ for C, N, O atoms, and by 10³ for H atoms. The equivalent temperature factors (Å²) are given in the last column. The numbering scheme of the atoms is shown in Fig. 2, and the H atoms are represented by the numbering of the attached C atoms.

	x	y	z	B _{eq}
N(1)	2124 (2)	-920 (2)	-478 (1)	3.1
N(4)	1266 (2)	1721 (2)	380 (1)	3.1
C(2)	2053 (3)	-792 (3)	177 (1)	3.1
C(3)	2485 (3)	734 (3)	374 (1)	3.3
C(5)	377 (3)	1459 (3)	892 (1)	3.3
C(6)	-1152 (3)	2006 (3)	754 (1)	3.4
C(21)	2940 (3)	-1921 (3)	539 (1)	4.6
C(22)	2634 (4)	-1989 (4)	1196 (1)	6.3
C(51)	1018 (3)	2042 (4)	1498 (1)	5.0
C(52)	345 (4)	1332 (5)	2026 (1)	8.0
C(11)	3576 (3)	-1095 (3)	-669 (1)	3.6
C(12)	3658 (3)	-681 (3)	-1316 (1)	3.6
C(13)	4277 (3)	-1571 (3)	-1717 (1)	4.9
C(14)	4328 (4)	-1188 (4)	-2316 (2)	6.3
C(15)	3782 (4)	94 (4)	-2513 (1)	6.1
C(16)	3176 (4)	1002 (4)	-2118 (1)	5.6
C(17)	3122 (3)	617 (3)	-1528 (1)	4.6
C(41)	1774 (3)	3208 (3)	359 (1)	3.7
C(42)	2100 (3)	3648 (3)	-266 (1)	3.7
C(43)	3475 (3)	4009 (3)	-399 (1)	4.6
C(44)	3751 (4)	4462 (3)	-971 (2)	5.7
C(45)	2658 (4)	4555 (3)	-1410 (1)	5.7
C(46)	1284 (4)	4186 (4)	-1284 (1)	5.5
C(47)	1009 (3)	3738 (3)	-715 (1)	4.5
H(11)	425 (2)	-41 (2)	-40 (1)	3.1 (0.5)
H(12)	400 (2)	-210 (2)	-60 (1)	3.5 (0.5)
H(13)	470 (3)	-249 (3)	-157 (1)	6.1 (0.7)
H(14)	482 (4)	-183 (4)	-257 (2)	8.7 (1.0)
H(15)	378 (3)	35 (4)	-295 (1)	7.8 (0.9)
H(16)	274 (3)	192 (4)	-227 (1)	8.3 (0.9)
H(17)	264 (3)	119 (3)	-126 (1)	5.2 (0.7)
H(21)	97 (2)	-92 (2)	26 (1)	3.2 (0.5)
H(22)	273 (3)	-285 (3)	36 (1)	4.2 (0.6)
H(23)	404 (3)	-174 (3)	51 (1)	6.6 (0.8)
H(24)	164 (3)	-212 (3)	129 (1)	7.4 (0.8)
H(25)	293 (4)	-111 (4)	143 (2)	9.7 (1.0)
H(26)	312 (4)	-283 (4)	139 (2)	9.5 (1.0)
H(31)	308 (3)	71 (3)	78 (1)	4.5 (0.6)
H(32)	316 (2)	116 (2)	8 (1)	3.1 (0.5)
H(41)	98 (2)	389 (3)	49 (1)	3.9 (0.6)
H(42)	269 (2)	337 (3)	66 (1)	4.2 (0.6)
H(43)	427 (2)	393 (3)	-8 (1)	4.7 (0.6)
H(44)	478 (3)	472 (3)	-105 (1)	6.9 (0.8)
H(45)	284 (3)	489 (3)	-180 (1)	7.2 (0.8)
H(46)	48 (3)	426 (3)	-160 (1)	5.6 (0.7)
H(47)	4 (3)	348 (3)	-63 (1)	4.9 (0.6)
H(51)	29 (2)	37 (2)	94 (1)	2.3 (0.4)
H(52)	205 (3)	183 (3)	154 (1)	5.0 (0.6)
H(53)	91 (3)	312 (3)	149 (1)	5.5 (0.7)
H(54)	-72 (4)	167 (4)	204 (2)	12.1 (1.2)
H(55)	73 (4)	181 (5)	241 (2)	12.0 (1.3)
H(56)	60 (3)	36 (3)	203 (1)	6.9 (0.8)
H(61)	-152 (2)	231 (2)	114 (1)	3.3 (0.5)
H(62)	-114 (2)	295 (3)	51 (1)	3.7 (0.5)

the 12-membered ring, the skeleton of the molecule appeared to be a distorted square ring with the methylene groups at the corners (Fig. 2a). However,

the two torsion angles at the C(6) corner are *gauche* and *-gauche*. The ring conformation then is quite different from the *RRRR*-type, and takes an armchair form with C(6') and C(6) at the top and the toe respectively (Fig. 2b). The torsion angles and the bond lengths and angles are shown in Fig. 3. The important torsion angles in the ring, together with those in the *RRRR*-type and TETA molecules, are compared in Table 2. The deviations of these torsion angles for the *RRSS*-type from the expected values of the *trans* and *gauche* conformations are larger than those of the others. The bond angles C(n+1)-C(n+1)1-C(n+1)2 (n = 1 or 4), of the ethyl groups, and N(n)-C(n)1-C(n)2 (n = 1 or 4), of the benzyl groups, are several degrees larger than the standard tetrahedral angle of 109.4°. Therefore, it is supposed that the strain energy of the present molecule is higher than that of the *RRRR*-type.

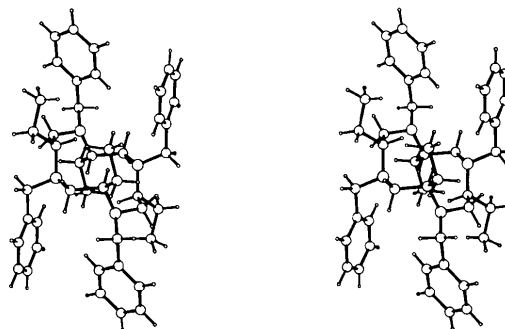


Fig. 1. A stereoscopic drawing of the molecule.

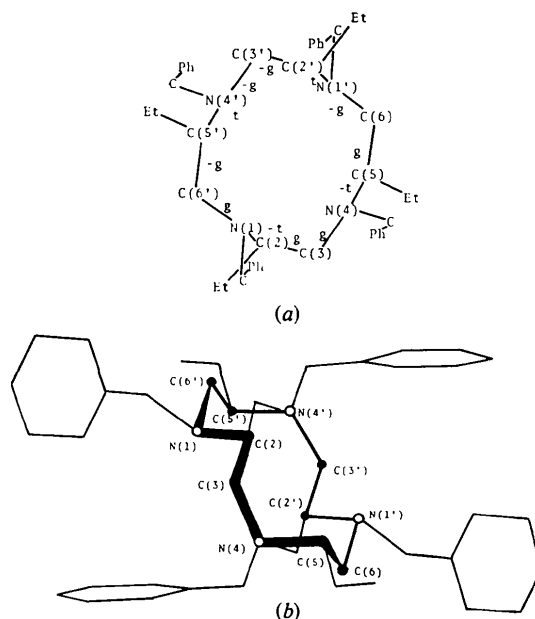


Fig. 2. The skeleton of the molecule. (a) The projection on the mean plane of the 12-membered ring. (b) The armchair view.

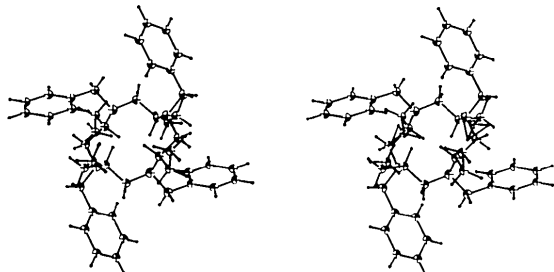


Fig. 5. A stereoscopic drawing of the molecular model at the subsidiary minimum *B*.

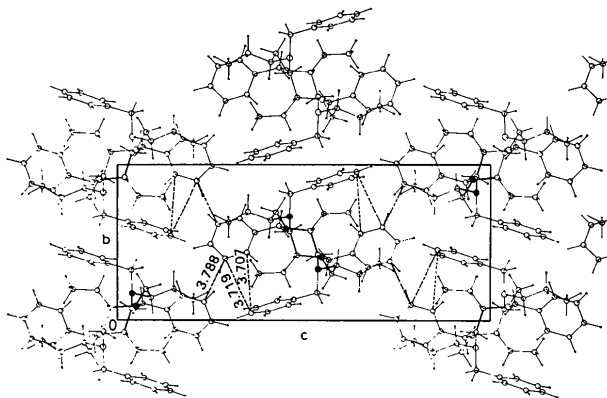


Fig. 6. Packing view of the crystal structure (*a*-axis projection).

The packing of the molecules in the crystal is shown in Fig. 6. None of the intermolecular C—C distances is shorter than 3.7 Å, and the main interactions are

between the phenyl groups, as shown by the broken lines in Fig. 6.

Calculations were performed on a FACOM 230-75 computer of this Institute using the *UNICS II* program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974) for crystallography, *LSAM* (Main, Woolfson & Germain, 1972) for the direct phasing, and *MMB* (Sakurai & Kobayashi, 1972; Sakurai, 1978) for the conformational-energy calculation.

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17β-Hydroxy-5α-androst-1-en-3-one Hydrate*

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Abstract. C₁₉H₂₈O₂·H₂O, *M_r* = 306.4, *ρ_x* = 1.194 Mg m⁻³, monoclinic, *P*2₁, *Z* = 2, *a* = 10.5592 (6), *b* = 7.8881 (4), *c* = 10.2462 (6) Å, β = 92.345 (5)°, *V* = 852.71 Å³. Final *R* = 0.058 for 1727 independent reflections. The 5α sofa conformation of the Δ¹-3-one *A* ring does not produce the type of convexity needed to explain the 1α stereoselectivity of methyl Grignard

addition. The C(19) angular methyl hydrogens provide a steric cover for the β face of C(1), blocking approach from this direction by the reagent, while the C(1) α face is relatively open to attack.

Introduction. Attempts to explain the stereospecificity of conjugate addition reactions to Δ¹-3-one steroids have produced much speculation about the *A*-ring conformations of the precursor molecules and the resulting C(1) alkylated steroids. For example, Kirk &

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