Instrumental Achievements

Crystal Structure of 2(*S*),5(*S*),8(*S*),11(*S*)-1,4,7,10-tetraethyl-2,5,8,11-tetraisobutyl-1,4,7,10-tetraazacyclododecane and Its Analog

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The title compound (**1** in Fig. 1) and another optically active cyclen involving more bulky *N*-substituents, 2(*S*),5(*S*),8(*S*),11(*S*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraisobutyl-1,4,7,10-tetraazacyclododecane (**2**), were prepared and characterized in connection with study of chiral cyclens.¹ In order to elucidate the stereochemistry of the compounds, the crystal structures were determined by X-ray analysis.

Colorless crystals of **1** (*m/z* 508, mp 145–146°C, $[\alpha]_D^{25} -210^\circ$ (*c* 0.1, benzene)) and **2** (*m/z* 756, mp 194–196°C, $[\alpha]_D^{25} -360^\circ$ (*c* 0.1, isooctane)) were obtained as a square rod from benzene and a plate from pentane, respective-

ly. The data were collected with graphite-monochromatized Mo K α radiation. No absorption correction was applied. Table 1 summarizes the crystal and experimental data. The absolute configuration was assigned based on the known configurations of the starting material. The H-atom coordinates were calculated assuming an ideal geometry. The anisotropic temperature factors for all non-H atoms and the isotropic temperature factors for H were applied; the weight was $4F_o^2/\sigma^2(F_o^2)$. In **2**, a few residual peaks between the molecules, assumed to be unstable solvent atoms, were not well defined. The temperature factors of these atoms were fixed in the refinement. The maximum height in the final difference Fourier map was $\Delta\rho_{\max}=0.31\text{ e}\text{\AA}^{-3}$ near to the solvent molecule and $\Delta\rho_{\min}=-0.29\text{ e}\text{\AA}^{-3}$. The final atomic parameters are given in Table 2.

Fig. 1 Chemical structure.

Table 1 Crystal and experimental data of **1** and **2**^a

Formula: C ₃₂ H ₆₈ N ₄ , C ₅₂ H ₇₆ N ₄
Formula weight = 508.90, 757.21
Crystal size = 0.25 × 0.20 × 0.08, 0.25 × 0.20 × 0.08 mm ³
Crystal system: monoclinic, monoclinic
Space group: <i>P</i> 2 ₁ , <i>P</i> ₂ <i>Z</i> = 2, 2
<i>a</i> = 10.641(1), 11.89(4) Å
<i>b</i> = 15.697(1), 12.195(9) Å β = 90.03(1), 107.1(1)°
<i>c</i> = 10.563(2), 19.05(1) Å
<i>V</i> = 1764.3(4), 2641(9) Å ³
<i>D_x</i> = 0.958, 0.952 Mg/m ³
μ for Mo K α = 0.052, 0.055 mm ⁻¹
<i>R</i> = 0.050, 0.095
No. of reflections used = 1803, 1242
Measurement: Rigaku AFC5S
Program system: TEXAN
Structure determination: Mithril ⁴
Refinement: full-matrix least-squares

a. The data of **2** placed after those of **1** in each row.Table 2 Final coordinates of non-hydrogen atoms
(a) Compound **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> /Å ²
N(1)	0.5478(3)	0	-0.0819(3)	3.4(2)
N(4)	0.5920(3)	0.0002(3)	0.2769(3)	3.3(2)
N(7)	0.2357(3)	0.0043(3)	0.3238(3)	3.3(2)
N(10)	0.1911(3)	0.0020(3)	-0.0355(3)	3.4(2)
C(2)	0.5846(4)	-0.0345(3)	0.0410(4)	3.2(2)
C(3)	0.5975(4)	0.0332(3)	0.1473(4)	3.4(2)
C(5)	0.4677(4)	-0.0340(3)	0.3141(4)	3.5(2)
C(6)	0.3658(4)	0.0351(3)	0.3283(4)	3.8(2)
C(8)	0.1968(4)	-0.0300(3)	0.1994(4)	3.5(2)
C(9)	0.1896(4)	0.0366(3)	0.0941(4)	3.4(2)
C(11)	0.3138(4)	-0.0339(3)	-0.0740(4)	3.2(2)
C(12)	0.4181(4)	0.0338(3)	-0.0873(4)	3.5(2)
C(13)	0.6350(4)	0.0640(4)	-0.1328(4)	4.5(3)
C(14)	0.6433(5)	0.0609(4)	-0.2747(5)	5.9(3)
C(15)	0.6410(4)	0.0652(3)	0.3654(4)	4.1(2)
C(16)	0.7831(5)	0.0630(4)	0.3718(5)	6.1(3)
C(17)	0.1495(4)	0.0706(4)	0.3704(4)	4.3(2)
C(18)	0.1462(5)	0.0736(5)	0.5152(5)	6.7(3)
C(19)	0.1428(4)	0.0647(4)	-0.1237(4)	4.4(3)
C(20)	-0.0007(5)	0.0681(5)	-0.1252(6)	7.2(4)
C(21)	0.7063(4)	-0.0876(3)	0.0322(5)	4.2(2)
C(22)	0.7075(5)	-0.1558(4)	-0.0715(5)	4.7(3)
C(23)	0.6131(6)	-0.2252(4)	-0.0479(6)	6.9(4)
C(24)	0.8379(6)	-0.1934(5)	-0.0861(7)	8.3(4)
C(25)	0.4761(4)	-0.0887(3)	0.4338(4)	4.1(2)
C(26)	0.5742(5)	-0.1590(4)	0.4318(5)	5.2(3)
C(27)	0.5493(7)	-0.2266(4)	0.3378(7)	8.6(4)
C(28)	0.5895(7)	-0.1979(5)	0.5637(7)	9.1(5)
C(29)	0.0748(4)	-0.0808(3)	0.2074(4)	3.8(2)
C(30)	0.0683(5)	-0.1485(3)	0.3118(5)	4.9(3)
C(31)	0.1639(6)	-0.2176(4)	0.2974(6)	7.0(4)
C(32)	-0.0615(6)	-0.1867(5)	0.3209(7)	9.1(4)
C(33)	0.3033(4)	-0.0890(3)	-0.1900(5)	4.3(3)
C(34)	0.2005(5)	-0.1570(4)	-0.1904(5)	5.4(3)
C(35)	0.2293(7)	-0.2277(4)	-0.0971(6)	7.9(4)
C(36)	0.1774(7)	-0.1923(5)	-0.3186(7)	8.9(4)

$$B_{eq} = (8\pi^2/3) \sum_i U_{ij}(a_i^* \cdot a_j^*)(a_i \cdot a_j).$$

Table 2 Final coordinates of non-hydrogen atoms
(b) Compound 2

Atom	x	y	z	B _{eq} /Å ²
N(1)	0.545(2)	0	0.708(1)	3(1)
N(4)	0.731(2)	-0.258(3)	0.717(1)	3(1)
N(7)	0.996(2)	-0.081(3)	0.708(1)	3(1)
N(10)	0.812(2)	0.176(2)	0.707(1)	2(1)
C(2)	0.610(2)	-0.104(2)	0.742(1)	2(1)
C(3)	0.632(2)	-0.179(3)	0.680(2)	4(2)
C(5)	0.849(2)	-0.208(3)	0.741(1)	4(2)
C(6)	0.897(2)	-0.159(3)	0.680(2)	3(2)
C(8)	0.959(2)	0.025(3)	0.737(2)	3(2)
C(9)	0.880(2)	0.095(3)	0.681(1)	2(1)
C(11)	0.722(3)	0.123(3)	0.739(2)	3(2)
C(12)	0.615(3)	0.077(3)	0.679(2)	5(2)
C(13)	0.436(3)	-0.017(3)	0.648(1)	3(2)
C(14)	0.340(4)	0.065(3)	0.627(3)	6(3)
C(15)	0.329(2)	0.132(4)	0.683(2)	4(2)
C(16)	0.242(3)	0.212(3)	0.667(2)	5(2)
C(17)	0.171(3)	0.218(4)	0.599(3)	7(3)
C(18)	0.185(4)	0.158(5)	0.538(3)	9(3)
C(19)	0.269(3)	0.085(4)	0.558(2)	8(2)
C(20)	0.724(2)	-0.346(3)	0.663(2)	5(2)
C(21)	0.622(2)	-0.428(3)	0.662(2)	3(2)
C(22)	0.588(3)	-0.448(3)	0.725(2)	6(2)
C(23)	0.500(4)	-0.527(4)	0.719(3)	7(3)
C(24)	0.456(4)	-0.578(4)	0.652(4)	8(3)
C(25)	0.493(5)	-0.560(5)	0.591(3)	9(3)
C(26)	0.576(3)	-0.480(4)	0.596(2)	4(2)
C(27)	1.053(3)	-0.062(4)	0.648(1)	5(2)
C(28)	1.131(2)	-0.161(3)	0.637(3)	4(2)
C(29)	1.190(3)	-0.233(4)	0.700(2)	6(2)
C(30)	1.258(4)	-0.312(4)	0.688(3)	8(3)
C(31)	1.275(3)	-0.325(3)	0.617(4)	8(3)
C(32)	1.222(3)	-0.258(4)	0.564(3)	8(3)
C(33)	1.147(3)	-0.173(4)	0.569(2)	6(2)
C(34)	0.761(2)	0.258(3)	0.653(2)	4(2)
C(35)	0.843(2)	0.347(3)	0.634(2)	4(2)
C(36)	0.941(3)	0.376(3)	0.695(2)	3(2)
C(37)	1.013(3)	0.457(4)	0.683(2)	6(2)
C(38)	0.993(4)	0.506(4)	0.614(3)	6(3)
C(39)	0.906(4)	0.472(4)	0.559(2)	6(2)
C(40)	0.825(3)	0.395(3)	0.568(2)	5(2)
C(41)	0.539(3)	-0.165(3)	0.783(2)	5(2)
C(42)	0.506(5)	-0.106(5)	0.840(3)	10(4)
C(43)	0.434(3)	-0.171(4)	0.877(2)	10(3)
C(44)	0.605(7)	-0.065(4)	0.897(3)	15(4)
C(45)	0.937(2)	-0.289(3)	0.788(2)	4(2)
C(46)	0.906(3)	-0.354(3)	0.845(2)	6(2)
C(47)	1.011(3)	-0.426(4)	0.887(2)	11(3)
C(48)	0.871(3)	-0.284(4)	0.899(2)	10(3)
C(49)	1.060(3)	0.085(4)	0.783(2)	5(2)
C(50)	1.151(7)	0.040(8)	0.835(4)	20(8)
C(51)	1.105(4)	-0.012(4)	0.890(3)	17(4)
C(52)	1.251(3)	0.105(4)	0.881(2)	8(2)
C(53)	0.684(3)	0.206(4)	0.786(2)	6(2)
C(54)	0.775(4)	0.254(4)	0.845(3)	9(3)
C(55)	0.737(4)	0.346(5)	0.892(3)	17(4)
C(56)	0.833(4)	0.182(6)	0.904(4)	17(5)
C(s)1	0.362(7)	0.43(1)	0.895(4)	31(3)
C(s)2	0.35(2)	0.51(2)	0.934(7)	39(7)
C(s)3	1/2	0.2(2)	1.0	30
C(s)4	1/2	0.7(2)	1.0	30
C(s)5	1/2	0.35(2)	1.0	30

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} (a_i^* \cdot a_j^*) (a_i \cdot a_j).$$

The molecular structures are shown in Fig. 2. Both molecules have an approximate C_4 symmetry, and the geometries are similar to that of 2(*S*),5(*S*),8(*S*),11(*S*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyltetraazacyclododecane (3).^{2,3} Thus, the conformations of the 12-membered ring take a square and crown type, the nitrogen atoms are situated at the corner, the equatorial *N*-substituents extend away from the cyclen ring, and the isobutyl groups stand axially from the ring plane.

When the 12-membered chiral cyclen ring takes a square conformation, there are three different possibilities according to the kind of corner atom: CH₂, CH and N.¹ Except for the case of 3, the CH₂ or CH corner conformations appear for all free bases and the

Fig. 2 Perspective view of 1 and 2 and atomic numbering. The hydrogen atoms are omitted.

corresponding protonated chiral cyclens so far determined. The *N*-corner conformation is probably common to those of free bases of *N*-substituted C_4 symmetry cyclen molecules.

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References

1. K. Kobayashi, S. Tsuboyama, K. Tsuboyama and T. Sakurai, *Acta Crystallogr.*, **C50**, 306 (1994).
2. T. Sakurai, K. Kobayashi, K. Tsuboyama and S. Tsuboyama, *Acta Crystallogr.*, **B34**, 3465 (1978).
3. T. Sakurai, K. Kobayashi, K. Kanari, T. Kawata, I. Higashi, S. Tsuboyama and K. Tsuboyama, *Acta Crystallogr.*, **B39**, 84 (1983).
4. C. J. Gilmore, *J. Appl. Cryst.*, **17**, 42 (1984).

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