

Polyoxamacrobicyclic Diamines. Structure of 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane and of its Bisborohydride, $C_{18}H_{36}N_2O_6 \cdot 2BH_3$

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The crystal structures of $C_{18}H_{36}N_2O_6 \cdot 2BH_3$ (I) and $C_{18}H_{36}N_2O_8$ (II) have been determined from diffractometer data by direct methods and refined by least-squares to R 0.054 [(I), 877 independent observed reflections] and 0.054 [(II), 1 774 independent observed reflections] respectively. (I) Exists in the *exo-exo*-conformation, while (II), which forms remarkably stable complexes with various metal cations, possesses the *endo-endo* conformation (*i.e.*, the lone pairs of the nitrogen atoms are both inside the molecular cavity). The values of the nonbonding $N \cdots N$ distance in both (I) and (II) are very close [6.76 (I), and 6.87 Å (II)]. The conformations of (I) and (II) can be related to those of bicyclic [8.8.8]hexacosanes corresponding to paths on the diamond lattice. Crystals of both compounds are monoclinic: (I), space group $C2/c$ with $a = 18.849(6)$, $b = 9.610(4)$, $c = 13.291(5)$ Å, $\beta = 102.25(6)^\circ$, $Z = 4$; (II), space group $P2_1/c$, $a = 16.832(7)$, $b = 7.450(3)$, $c = 16.921(8)$ Å, $\beta = 95.77(5)^\circ$, $Z = 4$.

AN ingenious synthesis has led to the production of macrobicyclic ligands with two nitrogen and several oxygen or other heteroatoms as potential donors.¹ It was found that these macroheterobicyclic diamines show a very strong tendency to form very stable complexes with various metal cations, leading to a new class of compounds called cryptates.² In these the cation is included within the central molecular cavity of the macrobicyclic. The structures of some of these complexes have been established by X-ray crystallography.³

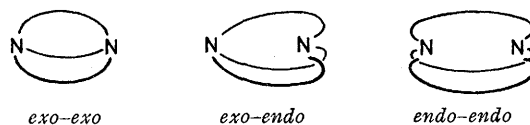
Like the macrobicyclic molecules of the [*k.l.m.*] type ($k, l, m \geq 6$) with nitrogen atoms at the bridgeheads, these molecules potentially can exist in various topologies related to the position of the nitrogen lone-pairs with

¹ (a) B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzat, *Tetrahedron*, 1973, **29**, 1629, and references therein; (b) B. Dietrich, J. M. Lehn and J. P. Sauvage, *Chem. Comm.*, 1970, 1055.

² B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron*, 1973, **29**, 1647, and references therein.

³ (a) B. Metz and R. Weiss, *Inorg. Chem.*, 1974, **13**, 2094, and references therein. (b) F. Mathieu and R. Weiss, *J.C.S. Chem. Comm.*, 1973, 816.

respect to the cavity defined by the bridges.^{4,5} For (II) n.m.r. spectral observations suggest two possible situations: a symmetrical form (*endo-endo* or *exo-exo*);^{1a} or an equilibrium mixture of three conformations, *endo-endo*, *endo-exo*, and *exo-exo*. In all the known cryptates of this ligand, its conformation is actually *endo-endo*.^{3a}

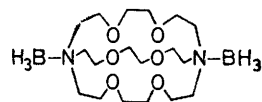


Since no structural determination of a free macrobicyclic diamine has yet been reported, we investigated the structure of (II) in order to study the conformation in the solid state. We also report the structure of an

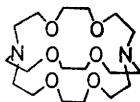
⁴ C. H. Park and H. E. Simmons, *J. Amer. Chem. Soc.*, 1972, **94**, 7184.

⁵ H. E. Simmons, C. H. Park, R. T. Uyeda, and M. F. Habibi, *Trans. New York Acad. Sci.*, 1970, **32**, 521, and references therein.

intermediate in the preparation of (II), namely the bisborohydride derivative (I) which was thought to be



(I)



(II)

forced in the *exo-exo* conformation and therefore interesting for comparison with the conformation of (II). A preliminary report of the structure of (II) has been published.⁶

$P2_1/c$ from systematic absences: $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). Cu- K_α radiation, $\lambda = 1.5418 \text{ \AA}$; $\mu(\text{Cu-}K_\alpha) = 6.63 \text{ cm}^{-1}$.

Unit-cell parameters were determined from precession photographs. Intensity data were then collected on a Pailred diffractometer with silicon-monochromated Cu- K_α radiation. A cylindrical crystal (diameter 0.45, length 1.0 mm) was oriented with its b axis along the ω axis of the instrument. All layers of reflections from $h0-6l$ were measured by the stationary-counter-moving-crystal method. The ω scan through reflections varied from 2.6° on the zero layer to 4.4° on the sixth layer with a scan speed of $2.5^\circ \text{ min}^{-1}$. Background was measured for 20 s on each side of a reflection with the counter and crystal both stationary.

TABLE I

Final positional and thermal parameters * for (I), with estimated standard deviations in parentheses

	x	y	z	β_{11}	β_{11}	β_{22}	β_{33}	β_{13}	β_{23}
N(1)	0.0953(1)	0.2459(3)	0.0939(1)	3.3(1)	16.5(6)	3.1(1)	0.2(2)	-0.1(1)	-0.5(2)
C(2)	0.0838(2)	0.0555(4)	0.1126(2)	4.4(2)	16.5(8)	5.2(2)	-0.4(2)	-1.4(1)	-0.9(3)
C(3)	0.1618(2)	-0.0383(4)	0.1363(2)	5.6(2)	17.7(8)	6.1(2)	1.7(3)	-1.8(1)	-3.1(3)
O(4)	0.1944(1)	0.0277(3)	0.2104(1)	4.6(1)	20.7(5)	4.6(1)	2.9(2)	-1.3(1)	-2.4(2)
C(5)	0.2752(2)	-0.0187(4)	0.2318(2)	3.9(1)	12.6(1)	4.4(1)	1.1(2)	-0.2(1)	-0.4(2)
C(6)	0.2976(2)	0.0643(4)	0.3110(2)	3.1(1)	18.1(7)	4.6(1)	1.4(2)	-0.4(2)	-0.8(3)
O(7)	0.3766(1)	0.0101(3)	0.3383(1)	3.4(1)	17.0(4)	4.5(1)	1.7(1)	-0.2(1)	-0.7(1)
C(8)	0.4016(2)	0.0706(4)	0.4166(2)	4.0(1)	16.5(7)	3.6(1)	1.5(2)	-0.5(1)	1.4(2)
C(9)	0.4470(2)	0.2458(4)	0.4176(2)	3.3(1)	19.4(8)	3.6(1)	1.0(3)	-0.4(1)	-0.1(2)
N(10)	0.3979(1)	0.4003(3)	0.3899(1)	2.9(1)	14.9(5)	3.2(1)	-0.5(2)	0.0(1)	0.0(2)
C(11)	0.4432(2)	0.5309(4)	0.3467(2)	4.0(1)	18.3(7)	4.5(1)	-2.7(3)	0.1(1)	0.6(3)
C(12)	0.4412(2)	0.4833(5)	0.2605(2)	4.8(2)	26.1(9)	5.0(2)	-2.3(3)	1.5(1)	-1.6(3)
O(13)	0.3618(1)	0.5101(3)	0.2233(1)	5.4(1)	26.5(6)	4.1(1)	2.9(2)	-0.3(1)	-0.4(2)
C(14)	0.3491(2)	0.4536(5)	0.1447(2)	5.9(2)	32.9(1.0)	4.1(2)	-4.4(4)	1.5(1)	-2.1(3)
C(15)	0.2632(2)	0.4653(6)	0.1187(2)	5.0(2)	35.5(1.0)	3.4(2)	2.4(4)	0.2(1)	0.0(3)
O(16)	0.2487(1)	0.4155(4)	0.0397(1)	4.1(1)	51.2(9)	4.8(1)	-2.1(3)	1.1(1)	-3.7(3)
C(17)	0.1690(2)	0.4367(6)	0.0053(2)	4.3(1)	42.5(1.3)	4.7(2)	-1.5(4)	0.9(1)	2.9(4)
C(18)	0.1201(2)	0.2703(5)	0.0154(2)	4.4(1)	30.8(1.0)	3.6(2)	1.1(3)	0.2(1)	-2.1(3)
C(19)	0.0241(2)	0.3520(4)	0.1037(2)	3.1(1)	21.9(7)	3.5(1)	0.4(3)	-0.3(1)	-0.1(3)
C(20)	0.0065(2)	0.3867(5)	0.1880(2)	4.6(2)	26.8(9)	4.2(1)	-1.4(3)	0.4(1)	-0.7(3)
O(21)	0.0654(1)	0.5005(3)	0.2283(1)	6.1(1)	18.2(5)	3.9(1)	-0.6(2)	-0.7(1)	0.4(2)
C(22)	0.1168(2)	0.4175(5)	0.2873(3)	3.4(1)	18.1(8)	5.6(2)	1.4(3)	0.2(1)	0.6(3)
C(23)	0.1724(3)	0.5521(5)	0.3259(2)	5.7(2)	18.1(8)	4.0(2)	2.5(3)	-0.4(1)	-0.5(3)
O(24)	0.2244(1)	0.4721(3)	0.3834(1)	3.1(1)	21.3(5)	6.8(1)	-0.5(2)	-0.9(1)	3.6(2)
C(25)	0.2838(2)	0.5878(5)	0.4203(3)	4.4(1)	20.2(8)	5.2(2)	1.0(3)	-0.1(1)	0.3(3)
C(26)	0.3558(2)	0.4781(5)	0.4522(2)	3.9(1)	18.9(8)	3.4(1)	-0.1(3)	-0.2(1)	-0.4(3)

	x	y	z	$B/\text{\AA}^2$	x	y	z	$B/\text{\AA}^2$	
H(2a)	0.058(2)	-0.004(4)	0.061(2)	7.0	H(15a)	0.238(3)	0.380(7)	0.156(3)	7.8
H(2b)	0.050(2)	0.048(4)	0.159(2)	7.0	H(15b)	0.229(2)	0.570(6)	0.131(2)	7.8
H(3a)	0.202(2)	-0.018(4)	0.096(2)	7.9	H(17a)	0.170(2)	0.486(4)	-0.052(2)	8.5
H(3b)	0.153(2)	-0.182(4)	0.141(2)	7.9	H(17b)	0.139(2)	0.527(4)	0.032(2)	8.5
H(5a)	0.306(2)	0.031(4)	0.187(2)	6.1	H(18a)	0.150(2)	0.167(3)	0.002(2)	7.3
H(5b)	0.280(2)	-0.153(4)	0.235(2)	6.1	H(18b)	0.073(2)	0.276(5)	0.028(2)	7.3
H(6a)	0.264(2)	0.025(4)	0.348(2)	6.3	H(19a)	-0.023(2)	0.298(4)	0.075(2)	6.3
H(6b)	0.290(2)	0.202(5)	0.307(2)	6.3	H(19b)	0.037(2)	0.481(4)	0.076(2)	6.3
H(8a)	0.436(2)	-0.023(4)	0.440(2)	6.2	H(20a)	0.010(2)	0.265(4)	0.222(2)	7.3
H(8b)	0.355(2)	0.091(4)	0.450(2)	6.2	H(20b)	-0.054(2)	0.447(4)	0.185(2)	7.3
H(9a)	0.491(2)	0.233(3)	0.387(2)	6.1	H(22a)	0.147(2)	0.330(6)	0.260(3)	6.8
H(9b)	0.471(2)	0.266(4)	0.475(2)	6.1	H(22b)	0.088(3)	0.381(7)	0.334(3)	6.8
H(11a)	0.498(2)	0.540(4)	0.369(2)	6.6	H(23a)	0.148(3)	0.638(7)	0.352(3)	7.0
H(11b)	0.416(2)	0.656(4)	0.358(2)	6.6	H(23b)	0.203(3)	0.614(7)	0.282(3)	7.0
H(12a)	0.455(2)	0.354(5)	0.253(2)	7.6	H(25a)	0.261(2)	0.654(7)	0.468(2)	7.1
H(12b)	0.471(2)	0.547(5)	0.232(2)	7.6	H(25b)	0.300(2)	0.681(5)	0.381(2)	7.1
H(14a)	0.376(3)	0.334(6)	0.131(3)	8.1	H(26a)	0.336(2)	0.391(5)	0.488(2)	6.1
H(14b)	0.363(4)	0.554(9)	0.110(4)	8.1	H(26b)	0.388(2)	0.563(4)	0.487(2)	6.1

* Anisotropic thermal parameters in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, all $\times 10^3$.

EXPERIMENTAL

Crystal Structure of C₁₈H₃₆N₂O₆

Crystal Data.—C₁₈H₃₆N₂O₆, $M = 376.5$. Monoclinic, $a = 16.832(7)$, $b = 7.450(3)$, $c = 16.921(8)$ \AA , $\beta = 95.77(5)^\circ$, $U = 2111.1 \text{ \AA}^3$, $D_c = 1.074$, $Z = 4$, D_m (pycnometric in diethyl ether) 1.07 ± 0.02 , $F(000) = 824$. Space group

The scintillation counter and pulse-height analyser were adjusted to accept 98% of the Cu- K_α peak. Instrumental and crystal instabilities were checked by periodic monitoring of three standard reflections, but the variations in their intensities during data collection were negligible.

⁶ R. Weiss, B. Metz, and D. Moras, Proc. 13th Internat. Conf. Co-ordination Chem., 1970, vol. II, p. 85, Poland.

Structure Determination.—An independent set of 2 609 diffraction intensities to $2\theta_{\max}$ 115° was collected and corrected for Lorentz and polarization effects. Absorption corrections were made on the basis of a cylindrical approximation. The structure was solved by the symbolic-addition procedure.⁷ The twenty-six nonhydrogen atoms were located on an *E* map computed from a phasing of 314 reflections. Least-squares refinement⁸ with isotropic temperature parameters gave *R* 0.164 for 1 774 reflections with $I > 3\sigma(I)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weight *w* taken as $1/\sigma^2(F_o)$. Atomic scattering factors were taken from ref. 9 for neutral atoms. At this

Crystal Structure of C₁₈H₃₆N₂O₆·2BH₃

Crystal Data.—C₁₈H₃₆N₂O₆·2BH₃, *M* = 404.2. Monoclinic, *a* = 18.849(6), *b* = 9.610(4), *c* = 13.291(5) Å, β = 102.25(6)°, *U* = 2352.7 Å³, *D_c* = 1.14, *Z* = 4, *F*(000) = 888. Space group *C2/c* or *Cc* from systematic absences: *hkl* (*h* + *k* = 2*n* + 1) and *h0l* (*l* = 2*n* + 1). Mo-*K_α* radiation, λ = 0.7107 Å; μ(Mo-*K_α*) = 0.88 cm⁻¹.

Intensity data were collected on a Paired diffractometer with graphite-monochromatized Mo-*K_α* radiation. A crystal was cut to a parallelepiped of dimensions 0.25 × 0.25 × 0.37 mm. The reciprocal levels *h*k0—16 were recorded by the ω scan technique. Of 3 169 recorded

TABLE 2

Final positional and thermal parameters* for (II), with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
N(1)	0.1774(1)	-0.0191(4)	0.3681(2)	1.8(1)	9.4(5)	5.7(2)	0.0(2)	0.3(1)	-0.0(3)
C(2)	0.1583(2)	-0.1427(5)	0.4275(3)	2.8(1)	10.5(6)	5.5(3)	0.0(3)	0.5(1)	1.4(4)
C(3)	0.1394(2)	-0.2750(5)	0.3668(3)	2.8(1)	9.7(6)	7.2(3)	0.7(3)	0.4(2)	0.7(4)
O(4)	0.0628(1)	-0.2792(3)	0.3300(2)	2.4(1)	9.2(4)	6.9(2)	0.1(2)	0.7(1)	-1.0(3)
C(5)	0.0406(2)	-0.3970(5)	0.2667(3)	3.3(1)	8.2(6)	6.0(3)	-0.2(3)	0.6(2)	-1.0(3)
C(11)	-0.1129(2)	0.0130(4)	0.2184(3)	2.1(1)	8.5(6)	5.3(2)	0.1(2)	0.1(1)	0.1(3)
C(12)	-0.1239(2)	0.1384(5)	0.2809(3)	2.6(1)	12.6(7)	6.1(3)	0.2(3)	0.0(2)	-0.9(4)
O(13)	-0.0617(1)	0.1385(3)	0.3650(2)	3.6(1)	8.8(4)	6.4(2)	0.1(2)	-0.4(1)	-0.4(3)
C(14)	-0.0402(2)	0.2747(5)	0.4005(3)	2.8(1)	10.5(6)	7.3(3)	0.2(3)	1.2(2)	-2.6(4)
C(15)	0.0275(2)	0.2621(6)	0.4814(3)	3.0(2)	15.8(9)	7.5(3)	-0.8(3)	1.6(2)	-4.5(4)
O(16)	0.0851(1)	0.2208(4)	0.4345(2)	2.8(1)	17.1(6)	6.0(2)	0.9(2)	1.3(1)	-0.3(3)
C(17)	0.1409(2)	0.1488(5)	0.5006(3)	3.0(1)	12.8(7)	6.0(3)	-0.7(3)	0.4(2)	-1.4(4)
C(18)	0.1963(2)	0.1001(5)	0.4425(3)	2.3(1)	9.4(6)	7.0(3)	-0.5(2)	0.0(2)	-0.8(4)
B(27)	0.2517(3)	-0.0534(7)	0.3246(4)	2.4(2)	15.4(9)	8.4(4)	0.7(3)	1.7(2)	0.1(5)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> /Å ²		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> /Å ²
H(2a)	0.2030	-0.1563	0.4916	3.6	H(14b)	-0.0820	0.3192	0.4319	4.2
H(2b)	0.1217	-0.1090	0.4608	3.6	H(15a)	0.0415	0.3668	0.5108	4.5
H(3a)	0.1640	-0.2805	0.3127	4.0	H(15b)	0.0270	0.1927	0.5312	4.5
H(3b)	0.1522	-0.3635	0.4172	4.0	H(17a)	0.1717	0.2287	0.5531	4.3
H(5a)	0.0649	-0.3860	0.2117	3.9	H(17b)	0.1224	0.0742	0.5360	4.3
H(5b)	0.0573	-0.4866	0.3166	3.9	H(18a)	0.2085	0.1745	0.4097	3.5
H(11a)	-0.1065	-0.0665	0.2627	3.1	H(18b)	0.2426	0.0653	0.4944	3.5
H(11b)	-0.0700	0.0240	0.1879	3.1	H(27a)	0.2871	-0.0940	0.3950	4.3
H(12a)	-0.1201	0.2256	0.2322	3.8	H(27b)	0.2380	-0.1081	0.2589	4.3
H(12b)	-0.1608	0.1272	0.3118	3.8	H(27c)	0.2684	0.0417	0.3121	4.3
H(14a)	-0.0348	0.3299	0.3305	4.2					

* See footnote to Table 1.

point a computed three-dimensional difference electron-density map revealed the positions of all the hydrogen atoms. Hence, least-squares refinement was continued with variable positional parameters for each hydrogen atom but with a fixed isotropic temperature factor *B_H* determined by the relation *B_H* = *B_C* + 2, where *B_C* is the isotropic temperature factor of the bonded carbon atom. Further refinement of atomic positions with anisotropic temperature factors for the nonhydrogen atoms reduced *R* to 0.054. The weighted factor $R' = \{[\sum w|\Delta F|^2 / \sum w|F_o|^2]^{1/2}\}$ was 0.065. A *p* value of 0.04 was used in the last cycle of refinement.¹⁰ A three-dimensional difference electron-density map computed at this stage showed no peaks >0.23 eÅ⁻³. Final positional and thermal parameters are presented in Table 1, along with their estimated standard deviations obtained from the inverse matrix. Atoms are labelled as indicated in Figure 1 of ref. 3a.

* An attempt was made by use of Germain, Main, and Woolson's MULTAN program (March 1974). The statistics unequivocally proved the structure to be centrosymmetric. The reasons for the discrepancy between MULTAN and the N.R.C. programs are not understood. We observed that the latter programs systematically give wrong statistics for centrosymmetric face-centred groups.

⁷ J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

independent reflections, 877, having $\sigma(I)/I < 0.33$ were used for the refinement, after Lorentz and polarization corrections. No absorption corrections were applied.

Structure Determination.—A statistical analysis of the observed normalized structure factors, $|E_{hkl}|$, indicated the structure to be noncentrosymmetric. A number of tangent refinements were made,¹¹ based on different origin-defining reflections, with phases determined by a symbolic-addition procedure. The *E* map computed from the most promising refinement yielded initial co-ordinates for twenty-eight atoms. Least-squares refinement with isotropic temperature parameters gave *R* 0.16. Since inspection of the molecular model suggested the presence of a two-fold axis, subsequent calculations were based on the centrosymmetric *C2/c* space group.* This model converged to *R* 0.136. A difference-Fourier map indicated the positions of all the

⁸ C. T. Prewitt, Fortran IV, A Crystallographic Least-squares Program, Report ORNL TM 305, Oak Ridge National Laboratory, Tennessee, 1966.

⁹ F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

¹⁰ P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

¹¹ F. R. Ahmed, Ed., Proc. 1969 Internat. Summer School Crystallographic Computing, Munksgaard, Copenhagen, 1970, p. 71.

hydrogen atoms. Further refinement of all positional parameters converged to R 0.095. Final least-squares refinement with variable positional and anisotropic thermal parameters for all nonhydrogen atoms but with the hydrogen parameters fixed at their previous values led to R 0.054 and

RESULTS AND DISCUSSION

The molecular structure of (I) has a crystallographic two-fold axis (Figure 1).¹² The molecule has the expected *exo-exo* conformation with the borohydride group

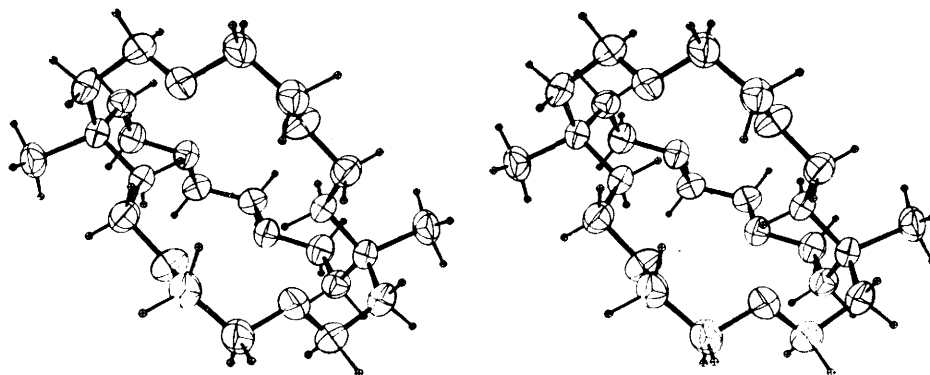


FIGURE 1 Stereoscopic view of the molecule of (I), with atoms shown as 50% probability ellipsoids for the thermal motion

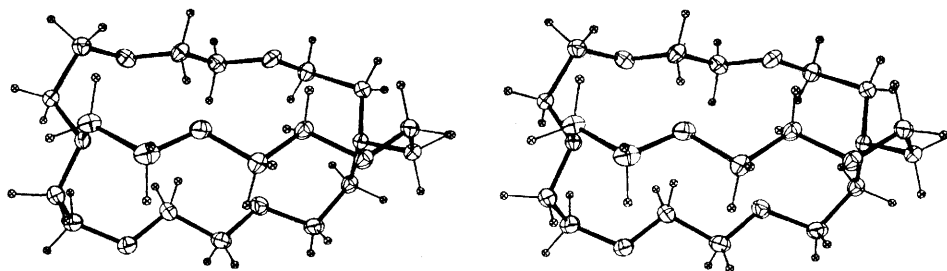


FIGURE 2 Stereodiagram of the molecule of (II) with the thermal ellipsoids at the 20% probability level

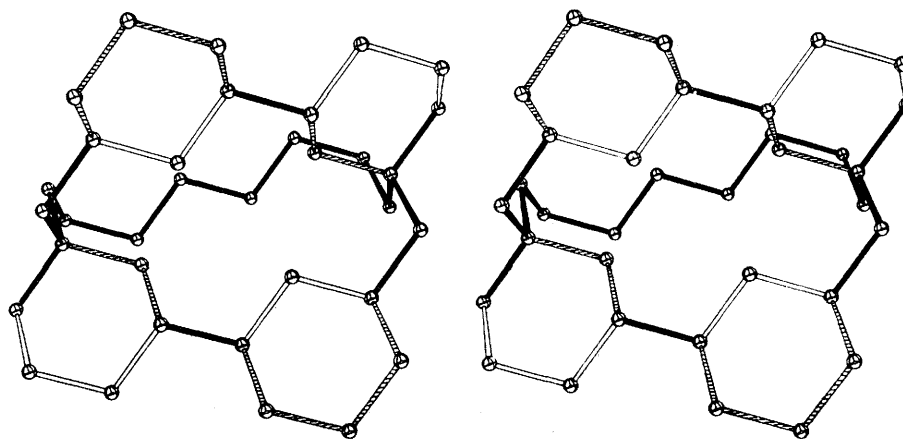


FIGURE 3 Stereodiagram of models *A* and *C* (see text). The shaded bonds are common to both, dashed ones belonging to *A* and the others to *C*

R' 0.060. A p value of 0.05 was used in the last cycles of refinement.¹⁰ The standard deviation of an observation of unit weight was 1.37. A final difference Fourier map revealed no peaks >0.18 e \AA^{-3} . Positional and thermal parameters from the output of the last cycle are listed in Table 2. Final observed and calculated structure factors for both (I) and (II) are listed in Supplementary Publication No. SUP 21564 (10 pp., 1 microfiche).*

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

directed outside the molecular cavity. The shortest intramolecular contacts (Table 3) across the cavity are O(16) \cdots C(19) 2.974(5), O(16) \cdots C(20) 3.201(5), and O(4) \cdots C(19) 3.074(5) \AA . The nonbonding distance between the two nitrogen atoms is 6.759(5) \AA .

A stereoview of the molecular structure of (II) is given in Figure 2. The molecule possesses a rugby football-

¹² C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Tennessee, 1965.

like shape. The conformer of (II) present in the crystalline state has the *endo-endo* conformation. The shortest contacts are: N(1) \cdots C(15) 3.255(4), N(10) \cdots C(6) 3.230(5), O(4) \cdots C(22) 3.488(4), and O(24) \cdots C(6) equal to 3.542(4) Å. As in (I) the oxygen lone pairs are available for interactions with other charges, since some of them point outside the cavity. The observed conformation implies that only small structural changes are required during the complex formation process, compared with the resulting situation in the cryptates.^{3a} With univalent cations, for example, the conformation

TABLE 3

Bond lengths and important intramolecular distances (Å)

(a) In (I)			
N(1)-C(2)	1.512(5)	N(1) \cdots O(4)	3.272(4)
C(2)-C(3)	1.507(6)	N(1) \cdots O(16)	3.126(4)
C(3)-O(4)	1.423(4)	N(1) \cdots O(21)	3.712(4)
O(4)-C(5)	1.419(5)	N(1) \cdots N(10)	6.759(5)
C(5)-C(6)	1.502(5)	O(4) \cdots O(7)	2.827(4)
C(11)-C(12)	1.503(6)	O(4) \cdots O(16)	4.995(4)
C(12)-O(13)	1.437(4)	O(4) \cdots O(21)	4.776(4)
O(13)-C(14)	1.421(5)	O(13) \cdots O(16)	2.838(4)
C(14)-C(15)	1.490(5)	O(13) \cdots O(24)	3.990(3)
C(15)-O(16)	1.419(5)		
O(16)-C(17)	1.402(5)		
C(17)-C(18)	1.498(6)		
C(18)-N(1)	1.506(5)		
N(1)-C(19)	1.517(4)		
N(1)-B(27)	1.657(6)		
(b) In (II)			
N(1)-C(2)	1.470(4)	C(22)-C(23)	1.482(4)
C(2)-C(3)	1.506(5)	C(23)-O(24)	1.377(4)
C(3)-O(4)	1.407(4)	O(24)-C(25)	1.416(4)
O(4)-C(5)	1.413(4)	C(25)-C(26)	1.516(4)
C(5)-C(6)	1.490(4)	C(26)-N(10)	1.448(4)
C(6)-O(7)	1.421(3)	N(1) \cdots O(4)	2.942(3)
O(7)-C(8)	1.422(3)	N(1) \cdots O(16)	3.094(3)
C(8)-C(9)	1.511(4)	N(1) \cdots O(21)	3.041(3)
C(9)-N(10)	1.466(4)	N(1) \cdots N(10)	6.871(4)
N(10)-C(11)	1.474(4)	N(10) \cdots O(7)	3.045(3)
C(11)-C(12)	1.499(5)	N(10) \cdots O(13)	2.940(3)
C(12)-O(13)	1.433(4)	N(10) \cdots O(24)	2.959(3)
O(13)-C(14)	1.390(4)	O(4) \cdots O(7)	3.572(3)
C(14)-C(15)	1.473(5)	O(4) \cdots O(16)	4.248(4)
C(15)-O(16)	1.374(4)	O(4) \cdots O(21)	4.164(3)
O(16)-C(17)	1.416(4)	O(7) \cdots O(13)	4.198(3)
C(17)-C(18)	1.506(5)	O(7) \cdots O(24)	4.402(4)
C(18)-N(1)	1.443(4)	O(13) \cdots O(16)	3.546(4)
N(1)-C(19)	1.458(4)	O(13) \cdots O(24)	3.744(4)
C(19)-C(20)	1.508(5)	O(16) \cdots O(21)	4.697(4)
C(20)-O(21)	1.424(4)	O(21) \cdots O(24)	3.560(3)
O(21)-C(22)	1.397(4)		

becomes more symmetrical (near D_3) by essentially changing the torsion angles around the central C-C bonds (Table 4). This in turn orients all oxygen atoms towards the centre of the cavity, making them available for the co-ordination of the cation and its stabilization.

The N(1) \cdots N(10) distance [6.871(4) Å] is very close to that found in (I), whereas in the corresponding cryptates it varies from 4.97 to 6.07 Å.^{3,13}

From the comparison of the structures two major features are apparent which will be discussed further. Both molecular structures can be roughly described as being part of a diamond lattice (Table 4), thus explaining why two opposite conformations of the same molecule lead to a similar nonbonding N \cdots N distance (Figure 3).

¹³ B. Metz, D. Moras, and R. Weiss, 2nd European Crystallographic Meeting, Hungary, 1974, p. 376.

Many other molecules of the same type which have been synthesized, may also follow the same structural rule.^{1,2,4,5} In any case, this assumption is reasonable in interpreting their structure.

TABLE 4

Torsion angles (°) *; estimated standard deviations all < 0.3°

(a) In (I)	A	B	C	D	Diamond lattice †		
					A	B	
B(27)-N(1)-C(2)-C(3)					-63	-g	a
B(27)-N(1)-C(18)-C(17)					-176	a	a
B(27)-N(1)-C(19)-C(20)					-61	-g	-g
N(1)-C(2)-C(3)-O(4)					-93	-g	g
C(2)-C(3)-O(4)-C(5)					176	-g	g
C(3)-O(4)-C(5)-C(6)					178	a	a
O(4)-C(5)-C(6)-O(7)					65	a	g
N(10)-C(11)-C(12)-O(13)					172	a	a
C(11)-C(12)-O(13)-C(14)					149	a	a
C(12)-O(13)-C(14)-C(15)					-176	a	a
O(13)-C(14)-C(15)-O(16)					70	g	g
C(14)-C(15)-O(16)-C(17)					-154	-g	-g
C(15)-O(16)-C(17)-C(18)					176	a	a
O(16)-C(17)-C(18)-N(1)					-73	a	a
C(17)-C(18)-N(1)-C(2)					-58	-g	-g
C(17)-C(18)-N(1)-C(19)					61	g	g
C(18)-N(1)-C(2)-C(3)					-178	a	g
C(18)-N(1)-C(19)-C(20)					59	g	g
C(2)-N(1)-C(19)-C(20)					178	a	a
C(19)-N(1)-C(2)-C(3)					60	g	-g
(b) In (II) ‡	A	B	C	D	Diamond lattice C		
N(1)-C(2)-C(3)-O(4)					-69	-g	
C(2)-C(3)-O(4)-C(5)					167	a	
C(3)-O(4)-C(5)-C(6)					-180	a	
O(4)-C(5)-C(6)-O(7)					-175	a	
C(5)-C(6)-O(7)-C(8)					175	a	
C(6)-O(7)-C(8)-C(9)					94	g	
O(7)-C(8)-C(9)-N(10)					-68	-g	
N(10)-C(11)-C(12)-O(13)					-69	-g	
C(11)-C(12)-O(13)-C(14)					173	-g	
C(12)-O(13)-C(14)-C(15)					-172	a	
O(13)-C(14)-C(15)-O(16)					-178	a	
C(14)-C(15)-O(16)-C(17)					174	a	
C(15)-O(16)-C(17)-C(18)					90	-g	
O(16)-C(17)-C(18)-N(1)					-76	-g	
N(1)-C(19)-C(20)-O(21)					-67	-g	
C(19)-C(20)-O(21)-C(22)					109	g	
C(20)-O(21)-C(22)-C(23)					178	a	
O(21)-C(22)-C(23)-O(24)					179	a	
C(22)-C(23)-O(24)-C(25)					-176	a	
C(23)-O(24)-C(25)-C(26)					155	a	
O(24)-C(25)-C(26)-N(10)					-68	-g	
C(2)-N(1)-C(18)-C(17)					152	a	
C(2)-N(1)-C(19)-C(20)					-73	-g	
C(18)-N(1)-C(2)-C(3)					-79	-g	
C(18)-N(1)-C(19)-C(20)					161	a	
C(19)-N(1)-C(2)-C(3)					156	a	
C(19)-N(1)-C(18)-C(17)					-82	-g	
C(9)-N(10)-C(11)-C(12)					-86	-g	
C(9)-N(10)-C(26)-C(25)					159	a	
C(11)-N(10)-C(9)-C(8)					145	a	
C(11)-N(10)-C(26)-C(25)					-72	-g	
C(26)-N(10)-C(9)-C(8)					-84	-g	
C(26)-N(10)-C(11)-C(12)					144	a	
(II)KI	(II)RbSCN·H ₂ O	(II)CsSCN·H ₂ O					
N-C-C-O	-56	65				70	
C-C-O-C	175	178				177	
O-C-C-O	51	65				70	
C-N-C-C	168	165				164	
	65	-74				-76	

* The torsion angle is positive if the sense of rotation from atoms BA to CD in projection down the bond BC is clockwise.
 † Gauche-bonds are represented by g, and anti-bonds by a.
 ‡ These values have been calculated with the $-x, -y, -z$ co-ordinates.

The shortest intramolecular contacts appear essentially in the borohydride derivative, thus indicating an overall less-stable conformation stabilized by the borohydride group. This implies that their removal induces a shift toward the *endo-endo* conformation which is most certainly the predominant one for the free ligand.

Torsion angles in (I) and (II) together with those of bicyclic [8.8.8]hexacosanes corresponding to bicyclic paths on the diamond lattice, are given in Table 4. For (I) two paths are possible. The corresponding models, called *A* and *B*, differ by the C(2)—(9) chain, due to the torsion angle around the C(5)—C(6) bond. The main differences between (I) and *A* exist for the C(2)—C(3)—O(4)—C(5), O(4)—C(5)—C(6)—O(7), C(14)—C(15)—O(16)—C(17), and O(16)—C(17)—C(18)—N(1) dihedral angles. In *A* the atoms from C(3) to (8) are coplanar, their plane being perpendicular to the two-fold axis.

The conformation of (II) is similar to that of model *C*. However, the values of the dihedral angles C(11)—C(12)—O(13)—C(14) and C(15)—O(16)—C(17)—C(18) are equal to 173 and 90°, respectively, while the corresponding ones in *C* are —g. Eleven other angles have deviations greater than 20°, the largest difference being 49° at C(19)—C(20)—O(21)—C(22). All mentioned deviations occur at C—X—C—C type angles (X = oxygen or nitrogen). This involves thirteen angles out of twenty-four. On the other hand, the agreement between the observed and theoretical values for the X—C—C—X type angles is remarkable, especially at the O—C—C—O angles. Dale¹⁴ pointed out for cycloalkanes and other flexible macrocycles that the replacement of a >CH₂ group by —O— does not disturb the conformation of the ring skeleton, so it would seem that the presence of the third chain causes most of the constraints. However, the conformations found in the crystal structures of (I) and (II) are likely to be the most stable, in view of their similarity with bicyclics described in the diamond lattice. Models *A* and *C* are represented in Figure 3. They can be superimposed in part. The nitrogen atoms are common, also chain C(11)—(18) of *C* with chain C(9)—(2) of *A*. The other chains do not have all atoms in common, owing to the presence of the —BH₃ groups.

The stereochemistry of the —BH₃ group is imposed by the size of the diborane molecule. Indeed, (I) is obtained from 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane-2,9-dione by reduction with diborane. The mechanism of the reduction is not known, but it is almost certain that the attack occurs on the unconstrained side. A molecular model of the diamide (CPK Precision Molecular Models) shows this to be quite difficult, if not impossible, from the inside of the cavity, since the —BH₃ groups are too bulky (to verify this we used the similar sized methyl group). One and even two methyl units can be forced inside the cavity of (II), but steric hindrances are very large and the three chains are strained.

Since the N—B is longer than the N—C bond, we think that two —BH₃ groups cannot get in together.

Bond distances and angles for non-hydrogen atoms are given in Tables 3 and 5. C—H distances, which vary from 0.87 to 1.11 Å in (I) and (II), are comparatively unreliable and expectedly short. The observed N—B bond distance [1.657(6) Å] may be compared with the values of 1.600(7) in H₃B·NH₂·[CH₂]₂·NH₂·BH₃,¹⁵ and 1.638 ± 0.010 in [CH₃]₃N·BH₃.¹⁶ A 'normal' bond dis-

TABLE 5

Bond angles (°)	
(a) In (I)	
C(2)—N(1)—C(18)	107.7(3)
C(2)—N(1)—C(19)	108.3(3)
C(2)—N(1)—B(27)	109.8(3)
C(18)—N(1)—C(19)	112.5(3)
C(18)—N(1)—B(27)	106.4(3)
C(19)—N(1)—B(27)	112.1(3)
N(1)—C(2)—C(3)	116.0(3)
C(2)—C(3)—O(4)	108.4(3)
C(3)—O(4)—C(5)	112.1(3)
O(4)—C(5)—C(6)	109.2(3)
N(10)—C(11)—C(12)	113.6(3)
C(11)—C(12)—O(13)	104.2(3)
C(12)—O(13)—C(14)	112.7(3)
O(13)—C(14)—C(15)	107.8(3)
C(14)—C(15)—O(16)	108.9(3)
C(15)—O(16)—C(17)	113.9(4)
O(16)—C(17)—C(18)	110.1(3)
C(17)—C(18)—N(1)	118.8(3)
(b) In (II)	
C(2)—N(1)—C(18)	112.1(2)
C(2)—N(1)—C(19)	111.7(2)
C(18)—N(1)—C(19)	110.7(3)
N(1)—C(2)—C(3)	112.0(2)
C(2)—C(3)—O(4)	109.1(2)
C(3)—O(4)—C(5)	114.9(2)
O(4)—C(5)—C(6)	106.2(3)
C(5)—C(6)—O(7)	108.6(2)
C(6)—O(7)—C(8)	113.1(2)
O(7)—C(8)—C(9)	112.7(2)
C(8)—C(9)—N(10)	113.9(2)
C(9)—N(10)—C(11)	111.9(2)
C(9)—N(10)—C(26)	112.5(2)
C(11)—N(10)—C(26)	114.4(2)
N(10)—C(11)—C(12)	111.3(2)
C(11)—C(12)—O(13)	108.8(2)
C(12)—O(13)—C(14)	115.2(2)
O(13)—C(14)—C(15)	109.1(3)
C(14)—C(15)—O(16)	110.7(2)
C(15)—O(16)—C(17)	115.8(3)
O(16)—C(17)—C(18)	111.6(3)
C(17)—C(18)—N(1)	114.8(2)
N(1)—C(19)—C(20)	116.2(3)
C(19)—C(20)—O(21)	111.2(2)
C(20)—O(21)—C(22)	115.2(2)
O(21)—C(22)—C(23)	109.2(2)
C(22)—C(23)—O(24)	110.2(2)
C(23)—O(24)—C(25)	114.7(3)
O(24)—C(25)—C(26)	109.3(2)
C(25)—C(26)—N(10)	112.9(2)

tance between four-co-ordinate nitrogen and four-co-ordinate boron is usually in the range 1.58 ± 0.02 Å.¹⁷ However, according to the acceptor character of the —BX₃ group, N—B distances up to 1.636(4) Å have been found.¹⁸

¹⁴ J. Dale, *J. Chem. Soc.*, 1963, 93.

¹⁵ H. Y. Ting, W. H. Watson, and H. C. Kelly, *Inorg. Chem.*, 1972, **11**, 374.

¹⁶ P. Cassoux, R. L. Kuczowski, P. S. Bryan, and R. C. Taylor, *Inorg. Chem.*, 1975, **14**, 126.

¹⁷ D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 2920.

¹⁸ P. S. Bryan and R. L. Kuczowski, *Inorg. Chem.*, 1971, **10**, 200, and references therein.

The mean B-H bond distance [1.03(8) Å] agrees with that found in the X-ray diffraction study of 6-B₁₀H₁₃NCS.¹⁹

Other observed bond lengths and angles in (I) and (II) are similar, *e.g.* the mean O-C 1.42, C-C 1.50 Å in (I), and 1.41 and 1.50 Å in (II); C-N-C 109, N-C-C 116, O-C-C 108, and C-O-C 113° in (I), *cf.* 112, 114, 110, and 115° in (II). An interesting feature is the lengthening

¹⁹ D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 2915.

of the N-C bond, induced by the adjacent N-B bond; in (II) the mean N-C is 1.459(4), and in (I) 1.507(5) Å. The presence of internal strain in (I) and (II) is evident from the values of the N-C-C and C-O-C angles.

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