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1,3,7,9,13,15,19,21-Octaazapentacyclo[19,3,1,1^{3,7},1^{9,13},1^{15,19}]octeicosane

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Abstract. C₂₀H₄₀N₈·C₆H₆. *M* = 470.5. Tetragonal, *P*4̄2₁*c*, *a* = 12.34 (2), *c* = 8.98 (1) Å from precession photographs, refined by diffractometer. *Z* = 2, *D_m* = 1.15 g cm⁻³ (floatation after coating with polyurethane), *D_c* = 1.17 g cm⁻³ (for the formula above). The compound was crystallized from benzene with the inclusion of molecules of solvent but rapidly lost these. The structure, refined to *R* = 0.073, consists of a 16-membered ring fused to four six-membered rings. The configuration, in which all atoms lie on points in the diamond lattice, is probably determined by dipole-dipole interactions.

Introduction. Systematic absences *hhl* *l* = 2*n* + 1, *h*00 *h* = 2*n* + 1 gave the space group uniquely as *P*4̄2₁*c*. Data were collected for layers *h*0*l* to *h*8*l* and *hk*0 to *hk*5 on a Hilger-Watts linear diffractometer (Mo *K*α radiation). Layer scales were found by comparing common reflexions, and the data were merged to give a set of 402 unique reflexions. The merging *R* [*R* = ∑(|*F*₁ - *F*₂)| / ½∑(*F*₁ + *F*₂))] was 0.047. Lorentz and polarization corrections were applied (but none for absorption). Throughout the data collection the crystal was kept in a thin-walled capillary. The structure was solved by Patterson methods, and all non-hydrogen atoms were

located, except those of the solvent. The atoms were refined by isotropic least-squares calculations and after three cycles a difference synthesis was calculated. This showed additional electron density around the special position ½, ½, 0, which has 4̄ symmetry. Stoichiometry requires one molecule of benzene at these positions so that the solvent molecules must be disordered, and this was roughly represented by fitting 12 half-carbon atoms [C(6), C(7), C(8)] to the electron density. Their isotropic temperature factors, but not their positions, were then refined. Hydrogen atoms were located from a difference synthesis and anisotropic temperature factors were introduced for the heavy atoms in the macrocyclic system. Refinement, including the positional parameters of the hydrogen atoms, converged at an *R* of 0.073 [where *R* = ∑(|*F*_o - |*F*_c|| / ∑|*F*_o|)].* The weighting scheme was: *F*_o ≤ 6, *w* = 1; *F*_o > 6, *w* = 1/[1 + (*F*_o - 6)²/9] and the scattering factors were taken from *International Tables for X-ray Crystallography* (1968). The programs used were our adaptations of the CRYSTAL

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30710 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positions and anisotropic temperature factors (× 10⁴)

The expression used for the anisotropic temperature factor was exp [-(β₁₁*h*² + β₂₂*k*² + β₃₃*l*² + 2β₁₂*hk* + 2β₁₃*hl* + 2β₂₃*kl*)] .

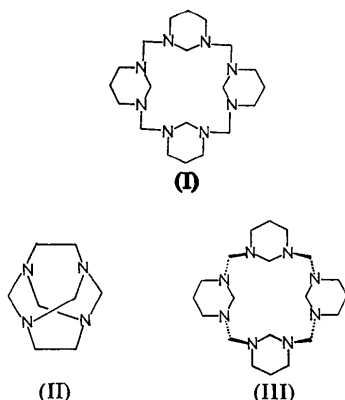
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
C(1)	1496 (5)	1651 (5)	910 (8)	76 (5)	78 (5)	146 (10)	-1 (4)	-14 (7)	-28 (7)
C(2)	162 (5)	2143 (5)	-970 (8)	81 (5)	62 (5)	122 (7)	11 (4)	12 (6)	16 (6)
C(3)	3498 (6)	-846 (6)	-699 (11)	72 (5)	112 (6)	252 (15)	10 (5)	-1 (8)	32 (9)
C(4)	3402 (5)	179 (7)	-1650 (9)	60 (4)	121 (7)	218 (12)	0 (5)	24 (8)	28 (9)
C(5)	2993 (5)	1125 (6)	-659 (9)	59 (4)	108 (6)	199 (12)	-16 (4)	15 (7)	14 (8)
N(1)	1983 (3)	788 (4)	55 (6)	51 (3)	73 (4)	132 (7)	-1 (3)	0 (5)	3 (5)
N(2)	1104 (4)	2504 (4)	-94 (7)	79 (4)	61 (3)	166 (9)	-6 (3)	4 (6)	5 (5)
C(6)*	5000	3870	0	141	141	273	*	*	*
C(7)	4000	4500	0	99	99	191	*	*	*
C(8)	4500	4000	0	99	99	191	*	*	*
H(1a)†	2039 (70)	1958 (63)	1538 (107)	112	112	216			
H(1b)	884 (61)	1290 (61)	1520 (94)	112	112	216			
H(2a)	2637 (66)	55 (78)	1864 (83)	104	104	200			
H(2b)	215 (57)	1541 (66)	-1509 (83)	104	104	200			
H(3a)	1617 (74)	3506 (74)	1503 (128)	136	136	264			
H(3b)	781 (68)	3947 (68)	31 (118)	136	136	264			
H(4a)	4187 (64)	367 (65)	-2098 (110)	132	132	254			
H(4b)	2770 (69)	126 (86)	-2575 (118)	132	132	254			
H(5a)	3654 (67)	1370 (66)	161 (123)	132	132	254			
H(5b)	2753 (67)	1748 (66)	-1492 (108)	132	132	254			

* Atoms C(6), C(7), C(8) were given occupancies of 0.5 and isotropic temperature factors. Their positions were not refined.

† Hydrogen atoms were assigned temperature factors (isotropic) related to the temperature factors of the carbon atom they were attached to. These were not refined.

69 system of Powell & Griffiths (1969). Atomic parameters are given in Table 1 and bond lengths, bond angles and torsional angles in the figure.

Discussion. A crystalline compound of formula $[(\text{CH}_2)_5\text{N}_2]$ can be isolated from the reaction of 1,3-diaminopropane and formaldehyde and its structure was suggested to be (I) on the basis of molecular weight measurements (Krassig, 1956). The corresponding product of reacting 1,2-diaminoethane and formaldehyde has been shown to be a dimer (Murray-Rust, 1974; Riddell & Murray-Rust, 1970) (II) and it was clearly of interest to confirm the structure of the title compound. This showed considerable variation in its n.m.r. spectrum as the temperature was changed, which suggested that ring and nitrogen inversions might be occurring (Riddell, 1971) and it was hoped that the structure of the crystalline benzene solvate might show the geometry of the most stable form.



The stoichiometry of the compound was assumed to be a 1:1 complex between the macrocycle and the benzene of crystallization, and this agreed reasonably well with both the density and the structure analysis. It was not felt necessary to introduce partial occupancy for this solvent molecule. The condensation product is confirmed as the tetramer and its structure is shown in Fig. 1. There are no intermolecular contacts between non-hydrogen atoms in the macrocycles of less than 3.9 Å, and as the benzene molecule has large thermal motion it is likely that intermolecular forces have a negligible effect on the shape of the macrocycle. This has $S_4(4)$ symmetry and neglecting the small deviations in bond lengths and angles all 28 heavy atoms can be superimposed on the diamond lattice. The 1,3-diazane rings each have one axial and one equatorially substituted nitrogen and as the torsional angles are all very close to 60 or 180° the molecule is almost free

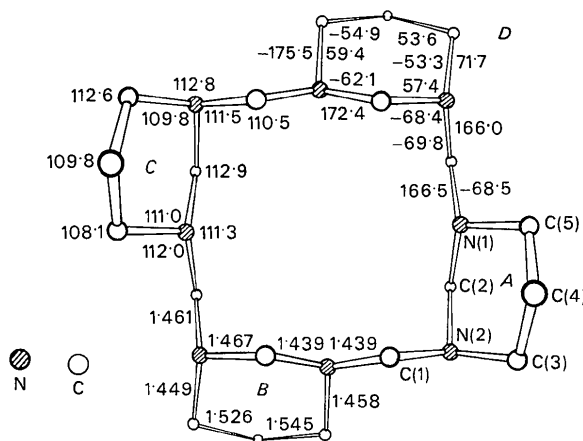


Fig. 1. The numbering of the atoms is shown in ring A, bond lengths (Å) in ring B, bond angles ($^\circ$) associated with C and torsional angles ($^\circ$) with D. The estimated standard deviations are approximately 0.008 Å for lengths, 0.4° for bond angles and 0.6° for torsional angles. The molecule is situated on a $\bar{4}$ symmetry element at 0, 0, 0 and the disordered benzene molecule (which is not shown) is at 0, 0, $\frac{1}{2}$ at a height of 4.49 Å above the centre of the macrocycle.

from strain. (There is a slight flattening of the diazane rings and the angles are mostly just greater than tetrahedral but the effect is not large.)

It is possible, however, to construct an alternative shape for the molecule (III) which is also strain-free and has all substituents equatorial. This isomer, which has D_{2d} symmetry, might be expected to be more stable as equatorial substituents are normally favoured in six-membered rings. However the dipole-dipole interactions between the lone pairs on the nitrogen atoms in this structure (the 'rabbit-ear' effect) are thought to be more serious (Eliel, 1969), and this would favour the structure actually observed.

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References

- ELIEL, E. L. (1969). *Kem. Tidskr.* pp. 22-27.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
 KRASSIG, H. (1956). *Makromol. Chem.* **17**, 77-89.
 MURRAY-RUST, P. (1974). *J. Chem. Soc. Perkin II*, pp. 1136-1141.
 POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69 system of crystallographic programs, Portsmouth Polytechnic.
 RIDDELL, F. G. (1971). Unpublished work.
 RIDDELL, F. G. & MURRAY-RUST, P. (1970). *Chem. Comm.* pp. 1075-1076.