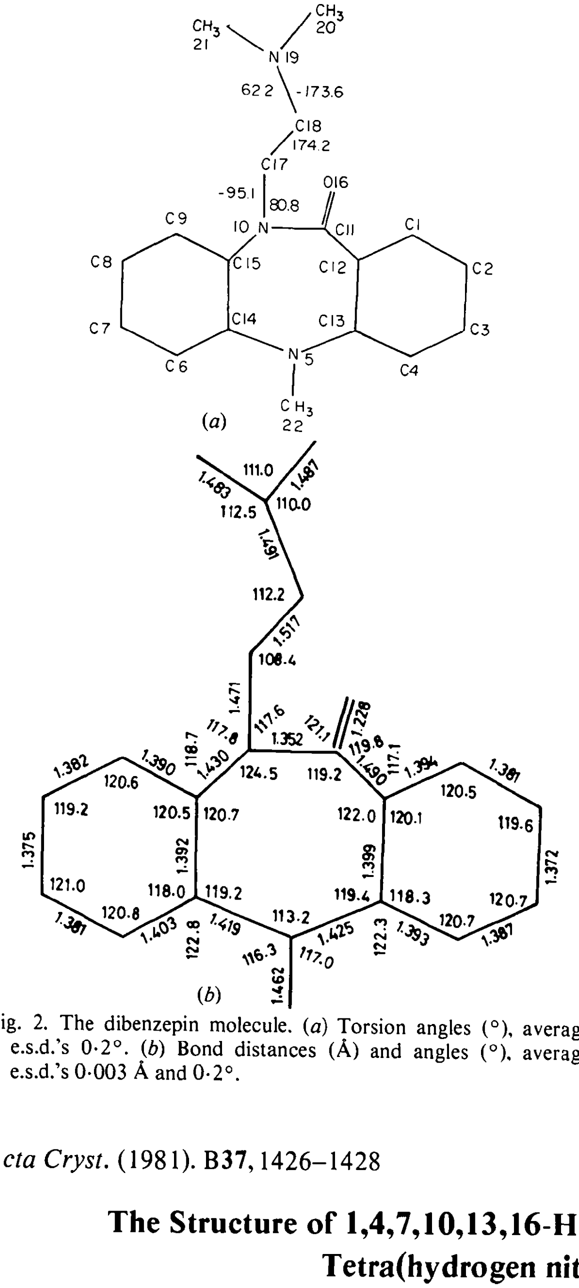

Fig. 2. The dibenzepin molecule. (*a*) Torsion angles (°), average e.s.d.'s 0·2°. (*b*) Bond distances (Å) and angles (°), average e.s.d.'s 0·003 Å and 0·2°.

From the pharmacological point of view, according to theories of structure–activity relations (Horn, 1976; Rodgers, Horn & Kennard, 1975), the distances from N(19) to the centers of the two phenyl rings may be important, these values being here 7·059 (1) and 5·485 (1) Å. The angle between the two phenyl rings also seems to be important (Maxwell, Keenan, Chaplin, Roth & Eckhardt, 1969), and in the present compound is 115·5 (2)°.

Most of the calculations were carried out with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Centro de Proceso de Datos del Ministerio de Educación, Madrid, for the facilities provided on the Univac 1108 computer.

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# The Structure of 1,4,7,10,13,16-Hexaazacyclooctadecane (Hexacyclen) Tetra(hydrogen nitrate) Dihydrochloride

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**Abstract.** $C_{12}H_{30}N_6.4HNO_3.2HCl$, triclinic, $P\bar{1}$, $a$ = 7·618 (7), $b$ = 10·583 (12), $c$ = 8·227 (7) Å, $\alpha$ = 106·60 (8), $\beta$ = 94·03 (7), $\gamma$ = 101·87 (9)°, $D_m$ = 1·58, $D_c$ = 1·57 Mg m$^{-3}$, $Z$ = 1, $V$ = 616 (1) Å$^3$. The structure was solved by direct methods and refined to $R$ = 0·046 for 1758 independent reflections. The 18-membered ring is centrosymmetric with no atom deviating by more than 0·76 Å from the least-squares plane.

**Introduction.** In the past several years few classes of compounds have been studied as extensively as the crown ethers, such as 18-crown-6 ether (I), and their derivatives (Poonia & Bajaj, 1979). Most of this work

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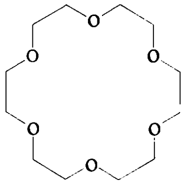
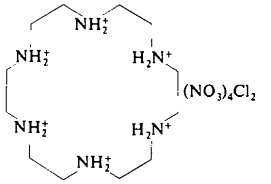
has been done with compounds containing six hetero atoms, generally four or more O atoms, the remainder being N and/or S atoms. In contrast, little is known about rings with six N atoms, the hexaamine counterparts of these crown ethers. In our investigations of hexaazacycloalkanes we have found that the 18-crown-6 N analog, 1,4,7,10,13,16-hexaazacyclooctadecane (hexacyclen) has many remarkable properties including oxyanion ($NO_3^-$, $ClO_4^-$ ...) complexation in aqueous acidic solution. This behavior has prompted us to study the crystal structures of hexacyclen acid salts.



(I)



(II)

Table 1. *Atomic coordinates with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$ trace **U**.

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$ × 10$^3$) |
|---|---|---|---|---|
| C(1) | 0·8487 (7) | 0·2809 (5) | −0·0609 (4) | 41 (3) |
| C(2) | 0·6630 (6) | 0·2945 (5) | −0·0164 (5) | 44 (3) |
| C(3) | 0·4904 (6) | 0·3670 (4) | 0·2272 (5) | 42 (3) |
| C(4) | 0·3405 (6) | 0·2399 (4) | 0·1867 (5) | 39 (3) |
| C(5) | 0·2222 (5) | 0·0227 (4) | 0·2436 (5) | 39 (3) |
| C(6) | 0·2777 (5) | −0·0753 (4) | 0·3276 (4) | 37 (3) |
| N(1) | 0·8411 (5) | 0·2152 (3) | −0·2498 (4) | 40 (3) |
| N(2) | 0·6678 (5) | 0·3454 (4) | 0·1727 (4) | 39 (3) |
| N(3) | 0·3710 (4) | 0·1502 (3) | 0·2916 (4) | 37 (3) |
| N(4) | 0·7204 (4) | 0·7242 (3) | 0·3010 (4) | 41 (3) |
| N(5) | 0·8272 (4) | 0·4741 (3) | 0·5953 (4) | 43 (3) |
| O(1) | 0·8468 (3) | 0·8179 (3) | 0·3902 (3) | 51 (2) |
| O(2) | 0·7435 (4) | 0·6448 (3) | 0·1627 (3) | 57 (3) |
| O(3) | 0·5680 (3) | 0·7065 (3) | 0·3520 (3) | 51 (3) |
| O(4) | 0·7662 (4) | 0·3489 (3) | 0·5192 (3) | 49 (2) |
| O(5) | 0·8144 (4) | 0·5565 (3) | 0·5162 (3) | 55 (3) |
| O(6) | 0·8979 (4) | 0·5122 (3) | 0·7475 (3) | 61 (3) |
| Cl | 0·2811 (1) | 0·9446 (1) | 0·7983 (1) | 43 (1) |
| HC1(1) | −0·095 (5) | 0·231 (4) | 0·005 (4) | 38 (10) |
| HC1(2) | 0·064 (5) | 0·630 (4) | 0·029 (4) | 49 (11) |
| HC2(1) | 0·383 (5) | 0·639 (4) | 0·057 (5) | 62 (13) |
| HC2(2) | 0·429 (4) | 0·794 (4) | 0·053 (4) | 43 (10) |
| HC3(1) | 0·519 (5) | 0·406 (4) | 0·342 (5) | 51 (11) |
| HC3(2) | 0·463 (5) | 0·429 (4) | 0·171 (5) | 54 (12) |
| HC4(1) | 0·330 (4) | 0·188 (3) | 0·068 (4) | 40 (10) |
| HC4(2) | 0·216 (5) | 0·262 (4) | 0·206 (5) | 67 (13) |
| HC5(1) | 0·204 (4) | −0·016 (3) | 0·117 (4) | 41 (10) |
| HC5(2) | 0·097 (4) | 0·045 (4) | 0·276 (4) | 50 (12) |
| HC6(1) | 0·414 (5) | 0·925 (4) | 0·321 (4) | 60 (12) |
| HC6(2) | 0·269 (5) | 0·953 (4) | 0·460 (5) | 64 (12) |
| HN1(1) | 0·190 (6) | 0·723 (4) | 0·302 (5) | 74 (15) |
| HN1(2) | 0·040 (6) | 0·781 (5) | 0·274 (6) | 91 (17) |
| HN2(1) | −0·286 (6) | 0·290 (5) | 0·222 (6) | 81 (17) |
| HN2(2) | −0·234 (5) | 0·424 (4) | 0·224 (5) | 60 (13) |
| HN3(1) | 0·376 (5) | 0·208 (4) | 0·422 (6) | 82 (14) |
| HN3(2) | 0·468 (6) | 0·128 (4) | 0·287 (5) | 69 (13) |

Crystals of hexacyclen.$4HNO_3$.2HCl (II) were prepared by recrystallizing hexacyclen.6HCl.$H_2O$ from either saturated $KNO_3$ or concentrated nitric acid solution. The crystal used for the X-ray study was grown slowly from nitric acid solution and was approximately 0·1 × 0·1 × 0·2 mm. Diffraction data ($2\theta$ max = 150°) were collected at room temperature on a computer-controlled Syntex $P2_1$ diffractometer operated in a $\theta$–$2\theta$ scan mode with a graphite monochromator and Cu $K\alpha$ ($\lambda$ = 1·54178 Å) radiation. No correction for absorption was made.

The structure was solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and difference syntheses. All H atoms were located from a difference map. In the final full-matrix least-squares calculation using atomic scattering factors from *International Tables for X-ray Crystallography* (1974) the heavy atoms were refined anisotropically and H atoms refined isotropically to $R$ = 0·046 for 1758 observed reflections. A final difference map showed no significant peaks. The positional parameters of the atoms are listed in Table 1.*

**Discussion.** The conformation of the hexaprotonated hexacyclen ring is shown in Fig. 1. Dihedral angles, interatomic distances and angles are given in Fig. 2. The ring, like that of 1,4,7,10,13,16-hexaoxacyclo-

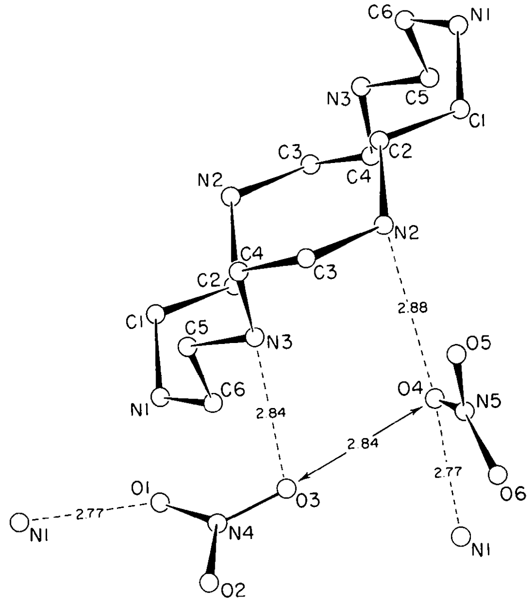


Fig. 1. Conformation of the hexacyclen ring with hydrogen-bonded nitrate ions. Dashed lines show N—H···O distances in Å. The solid line shows the non-bonded O(3)···O(4) approach. E.s.d.'s on the distances shown are ~0·005 Å.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35933 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

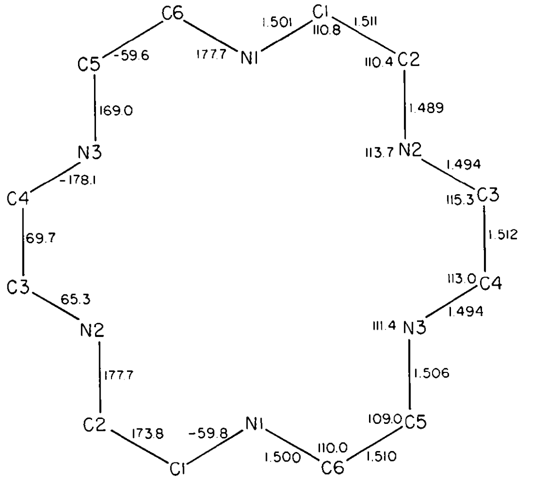

Fig. 2. Molecular geometry of the hexacyclen ring. The left-hand side of the diagram gives torsion angles (°) and the right-hand side gives bond distances (Å) and angles (°). E.s.d.'s of bond distances are approximately 0·005 Å, of bond angles 0·4°, and of torsion angles 0·6°.

octadecane, 18-crown-6 (Dunitz & Seiler, 1974), does not deviate markedly from its plane. In this case the average distance from the mean plane of C and N atoms is 0·44 Å with a maximum of 0·76 Å. The crystal structure contains a complex hydrogen-bonding network involving both the nitrate and chloride ions. The nitrate ions are attached to the 18-membered rings by strong N—H···O hydrogen bonds (Fig. 1) ranging from 2·77 Å to 2·88 Å for the N—O distances. This hydrogen bonding leads to a close approach between nitrate ions with O(3)···O(4) being 2·84 (1) Å apart. We are carrying out studies to investigate further the nature of the $NO_3^-$ hexacyclen interaction.

We are grateful to the staff of the University of Massachusetts Computer Center for their assistance.

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# α-L-Aspartylglycine Monohydrate

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**Abstract.** $C_6H_{10}N_2O_5.H_2O$, orthorhombic, $P2_12_12_1$, $a = 4{\cdot}844$ (5), $b = 9{\cdot}916$ (3), $c = 18{\cdot}070$ (4) Å, $V = 868{\cdot}05$ Å$^3$, $Z = 4$, $D_c = 1{\cdot}59$, $D_m$ (flotation in chloroform/iodoform) = 1·60 (1) Mg m$^{-3}$; $R_1 = 0{\cdot}040$, $R_2 = 0{\cdot}033$ for 1088 observations. The dipeptide crystallizes as a zwitterion with the main-chain carboxyl ionized and the side-chain amino group protonated. The overall dipeptide conformation is highly extended and the molecule is extensively hydrogen bonded.

**Introduction.** Colorless rods of α-L-aspartylglycine monohydrate were grown from aqueous ethanol at pH 6–7. A crystal of dimensions 0·125 × 0·300 × 0·525 mm was used in the analysis. Preliminary cell constants were obtained with the *SEARCH* routine on an Enraf–Nonius CAD-4 diffractometer. The crystals were assigned to the orthorhombic system; the observed systematic absences of $h00$ for $h$ odd, $0k0$ for $k$ odd, and $00l$ for $l$ odd indicated the noncentrosymmetric space group $P2_12_12_1$. Final cell constants (Mo $K\alpha$) were determined from a least-squares analysis of 25 reflections with $30° \le 2\theta(\text{Mo } K\alpha) \le 35°$ measured on the diffractometer. Intensity data were collected on the diffractometer in a $\theta$–$\omega$ scan mode, as suggested by the examination of the shapes of several peaks. A total of 1193 reflections with $2\theta \le 55°$ were collected and corrected for Lorentz–polarization effects but not for absorption since the small linear absorption coefficient ($\mu = 0{\cdot}154$ mm$^{-1}$) suggested to us that this effect is negligible. The programs used throughout the analysis were those provided by Enraf–Nonius with the CAD-4–SDP system.

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