

N—H bond lengths observed by neutron diffraction in this work are, as expected, significantly larger than those given by X-rays. Thus the previous discussion on the role of H in the telluric acid–glycine structure is supported by our present results.

The Te—O distances O—Te—O angles indicate substantial distortion of Te(OH)₆ groups from ideal octahedral coordination. As shown by X-rays, O(1) and O(3) participate in two longer Te—O bonds and are acceptors and donors of strong H bonds, N—H2(N)…O(1), Ow—H1(Ow)…O(1) and N—H(N)…O(3), whereas the O(2) atoms involved in the shorter Te—O(2) distances are acceptors of relatively weak H bonds (Table 3). The six O atoms in Te(OH)₆, all involved in H bonds, are both H-bond acceptors and donors. As donors they link the telluric acid group to four glycine molecules through strong bonds, O(1)—H(O1)…O(5), O(2)—H(O2)…O(4) and O(3)—H(O3)…O(5), and as H-bond acceptors they receive the electron excess from the water molecule, CH₂ and NH₃ groups.

In addition the C—H and N—H bonds observed in the glycine skeleton confirm the zwitterion form of this molecule; the bond lengths and bond angles characterizing the glycine molecule are, within e.s.d.'s, in good agreement with the values observed by neutron diffraction in the structure of α -glycine (Jönsson & Kvik, 1972).

Table 3. *Hydrogen-bond distances (Å) and angles (°) with their e.s.d.'s in parentheses*

<i>X—H…Y</i>	<i>X—H</i>	<i>X…Y</i>	<i>X—H…Y</i>
O(1)—H(O1)…O(5)	1.018 (9)	2.624 (6)	171.0 (8)
O(2)—H(O2)…O(4)	0.987 (12)	2.626 (7)	172.2 (9)
O(3)—H(O3)…O(5)	0.986 (11)	2.748 (7)	166.5 (8)
Ow—H(Ow)…O(5)	0.940 (15)	3.123 (8)	154.2 (1.2)
Ow—H1(Ow)…O(1)	0.950 (15)	2.935 (8)	163.3 (1.2)
N—H(N)…O(3)	1.027 (9)	2.979 (4)	162.8 (8)
N—H1(N)…O(w)	1.032 (10)	2.825 (7)	156.0 (8)
N—H2(N)…O(1)	0.992 (13)	2.984 (6)	153.7 (9)
C(2)—H1(C2)…O(2)	1.078 (11)	3.549 (8)	167.7 (7)
C(2)—H(C2)…O(2)	1.084 (9)	3.292 (8)	160.3 (7)

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Structure of 13,13'-[1,4-Phenylenebis(methylene)]bis-1,4,7,10-tetraoxa-13-azacyclopentadecane Dihydrochloride, a Bicyclic Macrocycle Containing Two [15]-NO₄ Subunits Linked by an Aromatic Group

BY J. REBIZANT

Commission of the European Communities, JRC Karlsruhe, Postfach 2266, D-7500 Karlsruhe, Federal Republic of Germany

M. R. SPIRLET

Laboratoire de Physique Expérimentale (B5), Université de Liège au Sart Tilman, B-4000 Liège, Belgium

AND P. P. BARTHELEMY AND J. F. DESREUX

Laboratoire de Chimie Analytique et de Radiochimie (B6), Université de Liège au Sart Tilman, B-4000 Liège, Belgium

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Abstract. C₂₈H₅₀N₂O₈²⁺.2Cl⁻, *M_r* = 613.6, monoclinic, *P*2₁/*c*, *a* = 9.873 (3), *b* = 10.823 (3), *c* = 15.823 (9) Å, β = 108.26 (4)°, *V* = 1606 (5) Å³, *Z* = 2, *D_x* = 1.269 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ =

2.468 cm⁻¹, *F*(000) = 660, *T* = 295 (1) K, final *R* = 0.034 for 1249 observed reflections. The title compound contains two identical monoaza tetraoxa 15-membered macrocycles linked by a *p*-xylylene bridge.

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As expected for odd-membered rings, the two binding subunits display an irregular geometry and only part of their conformational arrangement is found in the structures already reported for other 15-membered macrocycles. The molecular symmetry is $\bar{1} (C_i)$.

Introduction. Current interest in the coordination properties of macrocycles (Lehn, 1980) has stimulated the study of the solution and solid state conformations of these new ligands when they are either uncomplexed or chelated to a metal ion (Dale, 1980). The title compound contains two identical 15-membered rings bridged by an aromatic moiety; it is of special interest from two points of view. First, it contains odd-membered aza crowns and the conformation of these rings has been much less explored than that of the even-membered macrocycles. Odd-membered rings are not superimposable on the diamond structure and are likely to adopt a variety of distorted conformations of similar strain energies (Dale, 1973; Rubin, Williamson, Takeshita, Menger, Anet, Bacon & Allinger, 1984). Second, the title compound is a bis-macrocyclic that is potentially able to form dinuclear complexes and to encapsulate organic substrates, although it is far less rigid than the tricyclic cylindrical ligands whose structures have been reported previously (Pascard, Riche, Cesario, Kotzyba-Hibert & Lehn, 1982; Rebizant, Spirlet, Barthelemy & Desreux, 1984). The crystal structure of the title compound, hereafter designated as (I), is described in the present paper and its geometry is compared with the conformation exhibited by other similar macrocycles.

Experimental. The unprotonated form of (I) was obtained as a viscous oil according to a previously outlined procedure (Johnson, Sutherland & Newton, 1980). Crystals of (I) suitable for X-ray analysis were obtained in the course of NMR experiments. We happened to dissolve unprotonated (I) and twice an amount of *p*-aminoacetophenone hydrochloride in dry acetonitrile; proton exchange took place and colourless crystals were deposited within a few days. NMR spectroscopy and elemental analysis confirmed the chemical composition of the compound. Any attempt to obtain crystals directly from the dihydrochloride have failed presumably because (I) is only slightly soluble in acetonitrile.

Intensity data recorded at 295 (1)K on an Enraf-Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal dimensions: 0.30 × 0.15 × 0.16 mm; cell parameters refined by least squares from angle data for 25 reflections; systematic absences consistent with space group $P2_1/c$; 2823 unique reflections collected (θ - 2θ scan mode) in range $4 \leq 2\theta \leq 50^\circ$, h -12-12, k 0-13, l 0-19; intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean;

intensities corrected for Lorentz-polarization effects but not for absorption. Structure solved by direct methods and Fourier techniques. Full-matrix least-squares refinement with unit weights, minimizing $\sum(\Delta F)^2$. All H atoms located in subsequent difference electron density maps and refined isotropically. Non-H atoms refined anisotropically. 1249 independent reflections with $F^2 \geq 2\sigma(F^2)$; final $R = 0.034$ and $wR = 0.034$; $S = 0.886$, $(\Delta/\sigma)_{\max} = 0.01$; isotropic secondary-extinction coefficient refined to $g = 4.9868 \times 10^{-7}$ [$F_c = F_o/1 + g(F_o)^2Lp$]. Statistical analysis of R , wR and S in terms of data collection order, F_o , $\sin\theta/\lambda$ and classes of indices showed no unusual trends, indicating $w = 1$ to be an appropriate weighting scheme [the use of statistical weights, $w = 1/\sigma(F_o)^2$, led in this case to less satisfactory values for the R , wR and S agreement factors]. $\Delta\rho$ in final difference Fourier map within 0.139 and -0.172 e \AA^{-3} . Atomic scattering factors and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974); programs used are part of the Enraf-Nonius (1981) *Structure Determination Package*.

Discussion. The molecular structure of (I) is depicted in Fig. 1 together with the atom-labeling scheme. H atoms are omitted for the sake of clarity. The asymmetric unit contains half of the molecule that is centered on the $2(c)\bar{1}$ site (0, 0, $\frac{1}{2}$). The final fractional coordinates are reported in Table 1* and selected bond lengths are given in Table 2.

* Lists of structure-factor amplitudes, anisotropic thermal parameters, H-atom parameters and valency angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43607 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

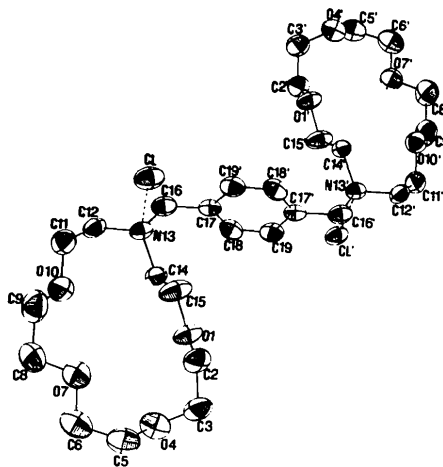


Fig. 1. Molecular geometry and labeling scheme. Atoms are depicted by their 50% probability ellipsoids.

The overall conformation of (I) can be described in terms of three molecular planes, namely the mean plane of the heteroatoms of each ring and the plane of the phenyl ring. These three planes are linked to one another by atoms C(16) and C(16').

The mean planes of the macrocycles are parallel; they are 0.398 (1) Å apart and are completely free of overlap. The dihedral angle between each macrocyclic mean plane and the phenyl plane is 76.5 (4)° while the angle between the axis C(17)–C(17') of the phenyl ring and each macrocyclic mean plane is 14.6 (4)°.

In the ammonium chloride group of each ring the N(13)···Cl distance of 3.065 (3) Å indicates a strong hydrogen bond with a bond angle N(13)–H(13)···Cl of 175 (2)°.

Atoms O(1) and O(7) are displaced on one side of the mean plane of the heteroatoms by 0.242 (2) and 0.368 (3) Å respectively, while atoms O(10) and O(4) are located on the other side of this plane and are 0.230 (3) and 0.347 (3) Å away from it; N(13) lies close to the mean plane.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$B_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\gamma B(1,2) + a\cos\alpha\cos\beta B(1,3) + b\cos\alpha\cos\beta B(2,3)].$$

	x	y	z	B _{eq}
Cl	0.2207 (1)	-0.26417 (9)	0.75607 (7)	4.83 (2)
O(1)	0.2956 (2)	0.2015 (2)	0.7671 (2)	4.55 (7)
O(4)	0.4355 (3)	0.3805 (3)	0.9020 (2)	5.32 (7)
O(7)	0.3819 (3)	0.1778 (3)	1.0059 (2)	6.14 (8)
O(10)	0.1333 (3)	0.0224 (3)	0.9423 (2)	4.87 (7)
N(13)	0.0237 (3)	-0.0406 (3)	0.7404 (2)	3.30 (7)
C(2)	0.4456 (4)	0.2137 (4)	0.8017 (3)	5.0 (1)
C(3)	0.4803 (4)	0.3454 (4)	0.8285 (3)	5.6 (1)
C(5)	0.5279 (4)	0.3404 (4)	0.9858 (3)	5.5 (1)
C(6)	0.4427 (5)	0.2932 (5)	1.0417 (3)	6.3 (1)
C(8)	0.3096 (5)	0.1222 (5)	1.0594 (3)	7.3 (1)
C(9)	0.2506 (5)	0.0014 (5)	1.0197 (3)	6.4 (1)
C(11)	0.0717 (4)	-0.0899 (4)	0.9024 (3)	4.9 (1)
C(12)	-0.0384 (4)	-0.0658 (3)	0.8142 (2)	4.01 (9)
C(14)	0.0949 (4)	0.0837 (3)	0.7494 (2)	3.55 (8)
C(15)	0.2497 (4)	0.0769 (4)	0.7602 (3)	5.5 (1)
C(16)	-0.0944 (4)	-0.0542 (4)	0.6526 (3)	4.1 (1)
C(17)	-0.0448 (3)	-0.0280 (3)	0.5739 (2)	3.38 (8)
C(18)	-0.0853 (4)	0.0797 (4)	0.5259 (2)	4.15 (9)
C(19)	-0.0423 (4)	0.1089 (3)	0.4535 (3)	4.15 (9)

Table 2. Bond lengths and selected intramolecular distances (Å)

O(1)–C(2)	1.415 (5)	C(2)–C(3)	1.496 (7)
C(3)–O(4)	1.420 (6)	O(4)–C(5)	1.420 (6)
C(5)–C(6)	1.489 (8)	C(6)–O(7)	1.424 (6)
O(7)–C(8)	1.402 (7)	C(8)–C(9)	1.488 (9)
C(9)–O(10)	1.416 (6)	O(10)–C(11)	1.415 (6)
C(11)–C(12)	1.499 (7)	C(12)–N(13)	1.504 (5)
N(13)–C(14)	1.504 (5)	N(13)–C(16)	1.515 (5)
C(14)–C(15)	1.485 (6)	C(15)–O(1)	1.416 (5)
C(16)–C(17)	1.502 (6)	C(17)–C(18)	1.379 (6)
C(18)–C(19)	1.379 (6)	C(19)–C(17')	1.388 (6)
N(13)···N(13')	7.526 (5)	O(1)···O(7)	3.613 (5)
N(13)···O(4)	6.109 (5)	O(4)···O(10)	5.052 (5)
O(1)···O(10)	4.098 (5)		

The conformation of the two 15-membered macrocycles of compound (I) is presented in Fig. 2 with the 'wedge' nomenclature already used elsewhere (Dale, 1973, 1980). The torsion angles are also included in Fig. 2 together with the *gauche*–*anti* symbols used by Dale (1980). In accordance with this author, the symbols *g*⁺ and *g*[–] denote angles in the range 0 ± 120° and *a* angles in the range 180 ± 60°. The symbols for angles close to 120° are enclosed in parentheses. As shown in Fig. 2, many dihedral angles are constrained to values that are far from 'ideal' and the overall conformation is strongly distorted. The cyclic subunits exhibit one 'genuine corner' *ag*⁺*g*⁺ [atoms C(5)–O(4)–C(3)–C(2)] and one 'pseudo corner' *ag*⁺*g*[–] [atoms O(10)–C(11)–C(12)–N(13)] with one close 1.5 H···O intramolecular interaction between O(10) and an H atom attached to C(14). However, several torsion angles are significantly different from the standard average values reported earlier (Dale, 1980).

To our knowledge, compound (I) is the first uncomplexed 15-membered aza crown macrocycle whose solid state structure has been determined. Thus, the overall conformation presented in Fig. 2 can only be compared with the geometries adopted by 15-membered macrocycles that are either coordinated to a metal ion or are hydrogen bonded to water molecules. For instance, the 15-crown-5 complex with BaBr₂ exhibits two conformations that are both very different from that of (I): one conformation displays a high symmetry and contains only *g*⁺*g*⁺*a* oxyethylene units while the other conformation is a less regular five-cornered (23343) structure (Feneau-Dupont, Arle, Declercq, Germain & Van Meersehe, 1979; Dale, 1980) that is characterized by successive groups of two, three, and so forth collinear bonds (Dale, 1980). If one limits oneself strictly to the 'wedge' nomenclature, one can find partial conformational sequences of (I) that have already been reported for other cyclopentadecane

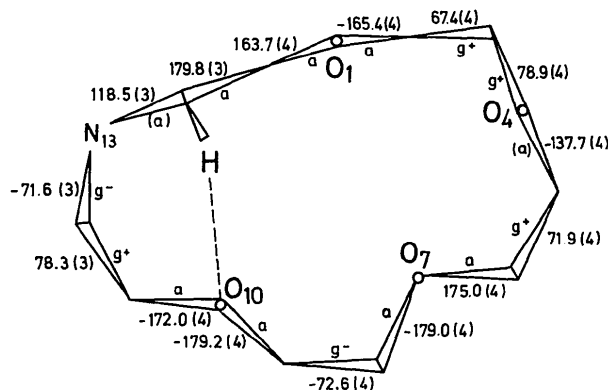


Fig. 2. 'Wedge' representation of the conformation of the macrocyclic subunits with torsion angles (°).

derivatives. For instance, (I) exhibits the $g^+aag^-aag^+ag^+g^+aa$ sequence that occurs in the sodium complex with 15-crown-5 or with *N*-phenyl-aza-15-crown-5 (Groth, 1981; Weber, Sheldrick, Dix & Vogtle, 1980). The same sequence is also exhibited by 15-crown-5 in an out-of-sphere complex with $CuBr_2 \cdot (OH_2)_2$ (Arte, Feneau-Dupont, Declercq, Germain & Van Meerssche, 1979). Moreover, (I) displays the smaller sequence $aag^-aag^+ag^+g^+a$ that is found in 15-crown-5 hydrogen bonded to an $Sm(ClO_4)_3$ complex (Lee, Sheu, Chiu & Chang, 1983). However, the analogy that one might draw from wedge representations is limited because of large differences (up to 39°) between the actual values of the torsion angles within the sequences that are apparently common to several rings. The exact geometrical arrangement of (I) is thus different from any other conformation reported to date including the structure suggested for uncomplexed 15-crown-5 in CS_2 on the basis of ^{13}C NMR studies (Dale, 1980).

The present crystallography analysis is entirely in keeping with earlier studies (Rubin *et al.*, 1984) indicating that odd-membered macrocyclic rings can adopt a variety of configurations.

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Scientifique of Belgium. JFD is Chercheur Qualifié and PPB is Aspirant at this Institution.

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Structure of Arprinocid [9-(2-Chloro-6-fluorobenzyl)adenine], a Coccidiostat

BY S. K. ARORA*

Drug Dynamics Institute, The University of Texas at Austin, Austin, Texas 78712-1074, USA

AND S. B. LARSON

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712-1074, USA

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Abstract. $C_{12}H_9ClFN_5$, $M_r = 277.69$, triclinic, $P\bar{1}$, $a = 8.715$ (2), $b = 11.210$ (2), $c = 7.435$ (1) Å, $\alpha = 92.5$ (1), $\beta = 121.8$ (1), $\gamma = 103.5$ (1)°, $V = 588.3$ Å³, $Z = 2$, $D_m = 1.568$, $D_x = 1.567$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 3.2$ cm⁻¹, $F(000) = 284$, $T = 163$ K, $R = 0.045$ for 2038 observed reflections. The substituted benzyl moiety is disordered into two orientations. The adenine moiety is almost planar with N(6) displaced by 0.04 Å from the nine-atom least-squares plane. The dihedral angle between the least-

squares planes of the adenine and substituted benzyl moieties has values of 86.2 and 87.8° (two orientations). The hydrogen bonding involves the usual N(6)—H...N(1) and N(6)—H...N(7) bonds.

Introduction. The veterinary use of drugs and antibiotics for the treatment of infectious diseases is based on similar principles to those in human medicine. Arprinocid, 9-(2-chloro-6-fluorobenzyl)adenine, is one of a class of 6-amino-9-(substituted)benzylpurines possessing broad-spectrum anticoccidial activity (Miller *et al.*, 1977). There has also been great interest in the

* Author to whom correspondence should be addressed.