

**Related literature.** The closest packing between chlorine atoms is Cl(1)···Cl(2), 3.88, Cl(1)···Cl(3), 3.85 and Cl(2)···Cl(3), 3.71 Å, in each case longer than the smallest possible distances calculated from the effective van der Waals radii of the Cl atom, 3.54, 3.36 and 3.40 Å respectively (Nyburg & Faerman, 1985).

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## Structure of 2,6-Pyrido-18-crown-6\*–Guanidinium Perchlorate–Deuteriochloroform

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**Abstract.**  $C_{15}H_{23}NO_5 \cdot CH_6N_3^+ \cdot ClO_4^- \cdot CDCl_3$ ,  $M_r = 577.27$ , orthorhombic,  $Pna2_1$ ,  $a = 10.799$  (1),  $b = 22.671$  (5),  $c = 10.561$  (2) Å,  $V = 2586$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.48$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu(Mo K\alpha) = 5.1$  cm<sup>-1</sup>,  $F(000) = 1200$ ,  $T = 168$  K, final  $R = 4.7\%$  for 1762 observed reflections. Each guanidinium cation is hydrogen-bonded to two 2,6-pyrido-18-crown-6 molecules, as the macrocyclic cavity of one crown molecule cannot encapsulate the cation completely. Similarly, each crown molecule is hydrogen-bonded with two cations. As a result, the structure consists of chains with an alternating sequence of crown molecules and cations. The perchlorate anion is involved in short contacts with two 2,6-pyrido-18-crown-6 molecules and one solvent molecule of deuteriochloroform.

**Experimental.** The title compound was obtained in an extraction experiment. A solution of 1 mmol of 2,6-pyrido-18-crown-6 in 2 ml  $CDCl_3$  was equilibrated with a solution of 2 mmol of guanidinium sulfate and 2 mmol  $LiClO_4$  in 2 ml  $H_2O$ . The organic layer was separated off and the amount of guanidinium perchlorate that was extracted into the organic phase was determined from the intensities in the <sup>1</sup>H NMR spectrum. Only 0.32 mmol of guanidinium perchlorate proved to be transferred. Upon addition of 0.5 ml of

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diethyl ether the complex crystallized and was filtered off; m.p. 353–356 K (Uiterwijk, van Staveren, Reinhoudt, den Hertog, Kruijs & Harkema, 1986).

Intensities were measured at 168 K on a Philips PW 1100 diffractometer (Mo  $K\alpha$  radiation, graphite monochromator). Lattice parameters determined by least squares from 25 centered reflections ( $4.5 < \theta < 9.5^\circ$ ). A total of 2404 independent reflections up to  $\theta = 25^\circ$  ( $0 \leq h \leq 12$ ,  $0 \leq k \leq 26$ ,  $0 \leq l \leq 12$ ) were measured in the  $\theta/2\theta$  scan mode (scan speed  $0.05^\circ$  s<sup>-1</sup>, scan width  $1.4^\circ$ ); 1762 reflections considered observed [ $F_o^2 > 3\sigma(F_o^2)$ ]. The intensity variation of three standard reflections, measured every hour, was less than 3%. No absorption correction.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. Weights for each reflection in the refinement (on  $F$ ) were calculated from  $w = 4F_o^2 / \sigma^2(F_o^2)$ ,  $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$ ; the value of the instability factor  $p$  was determined as 0.06. All H atoms were located on difference Fourier maps; they were placed in calculated positions and treated as riding on their parent atoms [bond distance 0.96 Å,  $B_{iso}(H) = 1.2 B_{eq}(\text{parent})$ ]. The number of parameters refined was 308: scale factor, isotropic extinction parameter [final value  $1.1(6) \times 10^{-7}$ ], positional and anisotropic thermal parameters for the non-H atoms.

Refinement converged at  $R = 4.7\%$ ,  $wR = 6.0\%$ ,  $(\Delta/\sigma)_{\max} = 0.11$ . Largest peak on final difference

\* IUPAC name: 3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1]-hencosa-1(21),17,19-triene.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms

	x	y	z	$B_{eq}(\text{\AA}^2)^*$
N(1)	0.0176 (4)	0.1164 (2)	-0.125	2.1 (1)
C(2)	-0.0207 (5)	0.0977 (3)	-0.0119 (6)	2.1 (1)
C(3)	0.0002 (5)	0.1354 (3)	0.1018 (6)	2.5 (1)
O(4)	0.0602 (4)	0.1884 (2)	0.0694 (4)	2.17 (8)
C(5)	0.0627 (6)	0.2282 (3)	0.1733 (6)	2.5 (1)
C(6)	0.1389 (6)	0.2806 (3)	0.1419 (6)	2.6 (1)
O(7)	0.0878 (3)	0.3092 (2)	0.0329 (4)	2.23 (8)
C(8)	0.1449 (6)	0.3652 (3)	0.0093 (7)	3.2 (1)
C(9)	0.1165 (6)	0.3859 (3)	-0.1190 (6)	2.9 (1)
O(10)	0.1901 (4)	0.3554 (2)	-0.2080 (5)	3.13 (9)
C(11)	0.1726 (7)	0.3756 (4)	-0.3349 (7)	3.9 (2)
C(12)	0.0645 (7)	0.3478 (3)	-0.3964 (8)	4.0 (2)
O(13)	0.0859 (5)	0.2856 (2)	-0.4044 (5)	3.5 (1)
C(14)	-0.0078 (8)	0.2578 (3)	-0.4756 (7)	4.0 (2)
C(15)	0.0169 (8)	0.1929 (3)	-0.4800 (6)	3.7 (2)
O(16)	-0.0107 (4)	0.1681 (2)	-0.3593 (4)	2.67 (9)
C(17)	0.0284 (6)	0.1075 (3)	-0.3522 (6)	2.9 (1)
C(18)	-0.0121 (6)	0.0829 (3)	-0.2275 (6)	2.4 (1)
C(19)	-0.0744 (6)	0.0312 (3)	-0.2188 (7)	2.9 (1)
C(20)	-0.1090 (6)	0.0104 (3)	-0.1008 (7)	3.1 (1)
C(21)	-0.0815 (5)	0.0435 (3)	0.0044 (7)	2.6 (1)
C(22)	0.3038 (5)	0.2169 (3)	-0.1192 (6)	2.0 (1)
N(23)	0.3905 (5)	0.2565 (2)	-0.1414 (5)	2.9 (1)
N(24)	0.2012 (4)	0.2150 (2)	-0.1860 (5)	2.4 (1)
N(25)	0.3236 (5)	0.1772 (2)	-0.0285 (5)	2.5 (1)
O(26)	0.3408 (1)	0.11371 (9)	0.3024 (2)	3.56 (3)
O(27)	0.2594 (5)	0.0912 (3)	0.2129 (6)	5.4 (1)
O(28)	0.3553 (8)	0.0770 (5)	0.4003 (9)	21.5 (5)
O(29)	0.2976 (8)	0.1660 (5)	0.341 (1)	22.7 (3)
O(30)	0.4549 (5)	0.1253 (4)	0.2585 (8)	7.8 (2)
C(31)	0.3411 (7)	-0.0207 (3)	-0.1577 (8)	3.4 (1)
Cl(32)	0.3314 (3)	0.02243 (9)	-0.0225 (2)	5.25 (5)
Cl(33)	0.3410 (2)	0.02307 (9)	-0.2963 (2)	4.52 (4)
Cl(34)	0.2204 (2)	-0.07219 (9)	-0.1626 (2)	4.47 (4)

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

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for non-H atoms, torsion angles ( $^\circ$ ) in the macrocycle and selected non-bonded distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

N(1)-C(2)	1.333 (7)	C(15)-O(16)	1.425 (8)	
N(1)-C(18)	1.361 (7)	O(16)-C(17)	1.439 (8)	
C(2)-C(3)	1.49 (1)	C(17)-C(18)	1.495 (9)	
C(2)-C(21)	1.403 (9)	C(18)-C(19)	1.356 (9)	
C(3)-O(4)	1.406 (8)	C(19)-C(20)	1.38 (2)	
O(4)-C(5)	1.422 (7)	C(20)-C(21)	1.37 (1)	
C(5)-C(6)	1.48 (1)	C(22)-N(23)	1.319 (8)	
C(6)-O(7)	1.432 (8)	C(22)-N(24)	1.315 (7)	
O(7)-C(8)	1.434 (8)	C(22)-N(25)	1.332 (8)	
C(8)-C(9)	1.47 (1)	Cl(26)-O(27)	1.388 (6)	
C(9)-O(10)	1.412 (9)	Cl(26)-O(28)	1.34 (1)	
O(10)-C(11)	1.429 (9)	Cl(26)-O(29)	1.34 (1)	
C(11)-C(12)	1.48 (2)	Cl(26)-O(30)	1.342 (7)	
C(12)-O(13)	1.431 (8)	C(31)-Cl(32)	1.734 (8)	
O(13)-C(14)	1.42 (1)	C(31)-Cl(33)	1.767 (8)	
C(14)-C(15)	1.50 (2)	C(31)-Cl(34)	1.751 (7)	
C(2)-N(1)-C(18)	117.5 (6)	N(1)-C(18)-C(17)	115.1 (6)	
N(1)-C(2)-C(3)	119.4 (5)	N(1)-C(18)-C(19)	123.1 (6)	
N(1)-C(2)-C(21)	122.3 (6)	C(17)-C(18)-C(19)	121.8 (6)	
C(3)-C(2)-C(21)	118.4 (6)	C(18)-C(19)-C(20)	119.4 (6)	
C(2)-C(3)-O(4)	111.3 (5)	C(19)-C(20)-C(21)	118.9 (7)	
C(3)-O(4)-C(5)	111.2 (5)	C(2)-C(21)-C(20)	118.8 (6)	
O(4)-C(5)-C(6)	110.3 (5)	N(23)-C(22)-N(24)	121.7 (5)	
C(5)-C(6)-O(7)	109.2 (5)	N(23)-C(22)-N(25)	118.2 (5)	
C(6)-O(7)-C(8)	112.0 (5)	N(24)-C(22)-N(25)	120.1 (5)	
O(7)-C(8)-C(9)	110.7 (5)	O(27)-Cl(26)-O(28)	111.9 (6)	
C(8)-C(9)-O(10)	109.9 (5)	O(27)-Cl(26)-O(29)	108.2 (5)	
C(9)-O(10)-C(11)	113.1 (6)	O(27)-Cl(26)-O(30)	114.7 (4)	
O(10)-C(11)-C(12)	112.3 (6)	O(28)-Cl(26)-O(29)	111.0 (8)	
C(11)-C(12)-O(13)	108.6 (6)	O(28)-Cl(26)-O(30)	106.4 (5)	
C(12)-O(13)-C(14)	111.0 (5)	O(29)-Cl(26)-O(30)	104.5 (5)	
O(13)-C(14)-C(15)	109.3 (6)	Cl(32)-C(31)-Cl(33)	111.4 (4)	
C(14)-C(15)-O(16)	108.8 (5)	Cl(32)-C(31)-Cl(34)	110.8 (4)	
C(15)-O(16)-C(17)	111.2 (5)	Cl(33)-C(31)-Cl(34)	110.5 (4)	
O(16)-C(17)-C(18)	108.4 (6)	C(17)-C(18)-N(1)-C(2)	177.4 (5)	
C(18)-N(1)-C(2)-C(3)	-174.8 (5)	C(9)-O(10)-C(11)-C(12)	-83.8 (7)	
N(1)-C(2)-C(3)-O(4)	0.3 (7)	O(10)-C(11)-C(12)-O(13)	-62.6 (8)	
C(2)-C(3)-O(4)-C(5)	170.8 (5)	C(11)-C(12)-O(13)-C(14)	-173.1 (6)	
C(3)-O(4)-C(5)-C(6)	173.4 (5)	C(12)-O(13)-C(14)-C(15)	-179.2 (6)	
O(4)-C(5)-C(6)-O(7)	59.2 (6)	O(13)-C(14)-C(15)-O(16)	73.3 (7)	
C(5)-C(6)-O(7)-C(8)	170.7 (5)	C(14)-C(15)-O(16)-C(17)	-171.5 (6)	
C(6)-O(7)-C(8)-C(9)	164.6 (5)	C(15)-O(16)-C(17)-C(18)	-175.6 (5)	
O(7)-C(8)-C(9)-O(10)	-77.1 (6)	O(16)-C(17)-C(18)-N(1)	-49.7 (7)	
Donor atom, D	Acceptor atom, A	Distance D...A	Distance H...A	Angle D-H...A
N(23)	O(4)	3.143 (7)	2.338 (5)	141.0 (3)
N(23)	O(7)	3.186 (7)	2.395 (5)	139.4 (3)
N(23)	O(16)	3.059 (7)	2.255 (4)	140.7 (3)
N(24)	N(1)	3.057 (7)	2.099 (5)	175.5 (4)
N(24)	O(13)	3.072 (7)	2.172 (5)	155.6 (3)
N(25)	O(7)	2.942 (6)	2.061 (4)	152.0 (3)
C(3)	O(27)	3.197 (8)	2.381 (6)	142.7 (4)
C(20)	O(28 <sup>b</sup> )	3.32 (1)	2.482 (9)	145.2 (5)
C(31)	O(30 <sup>b</sup> )	3.36 (2)	2.517 (8)	146.2 (5)

Symmetry code: (i)  $-\frac{1}{2}+x, \frac{1}{2}-y, z$ ; (ii)  $-x, -y, -\frac{1}{2}+z$ ; (iii)  $1-x, -y, -\frac{1}{2}+z$ .

Fourier map  $0.4 \text{ e \AA}^{-3}$ . All calculations were performed using *SDP* (B. A. Frenz & Associates Inc., 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); D of  $\text{CDCl}_3$  taken as an H atom. Atomic parameters of non-H atoms are in Table 1.\* Bond distances and angles,

\*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44202 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

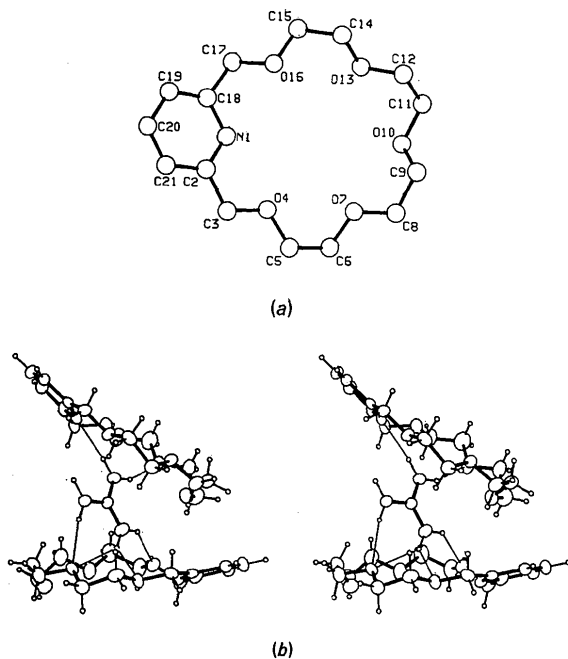


Fig. 1. (a) Atom numbering in 2,6-pyrido-18-crown-6. (b) Stereoscopic view of the structure, showing hydrogen bonds (thin lines) between the guanidinium cation and two (symmetry-related) macrocycles; the perchlorate anion and the deuteriochloroform molecule are omitted.

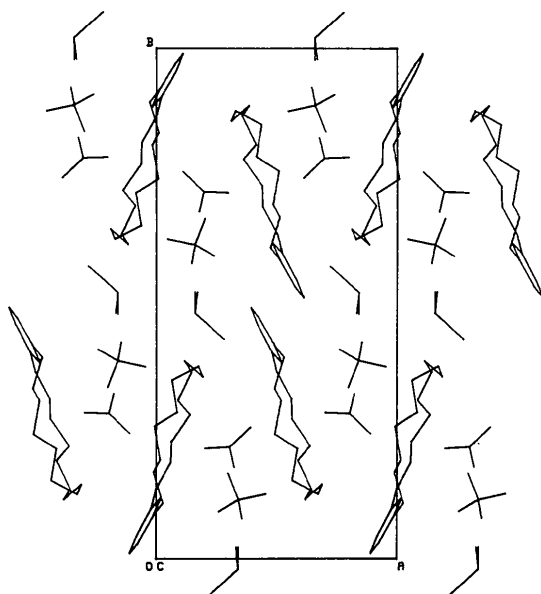


Fig. 2. Unit-cell contents; H atoms omitted for clarity.

torsion angles in the macrocycle and selected non-bonded distances and angles are in Table 2. Atom numbering in the macrocycle is shown in Fig. 1(a); guanidinium [C(22)–N(25)], perchlorate [Cl(26)–O(30)] and deuteriochloroform [C(31)–Cl(34)] are not shown. A stereoscopic view of the complex, showing hydrogen bonds, is in Fig. 1(b). Unit-cell contents are in Fig. 2.

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## Structure of 3-Amino-1*H*-indazole–Di-*tert*-butyl Fumarate Adduct

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**Abstract.** C<sub>19</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>, *M<sub>r</sub>* = 359.4, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 11.197 (2), *b* = 11.257 (2), *c* = 16.407 (3) Å, β = 100.59 (2)°, *V* = 2033 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.20 (5), *D<sub>x</sub>* = 1.174 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.897 cm<sup>-1</sup>, *F*(000) = 768, *T* = 293 (1) K, final *R* = 0.049 for 1560 observed reflexions. The adduct crystallizes as di-*tert*-butyl 2-(1*H*-indazol-3-yl)amino-fumarate. The indazole part of the molecule is planar to within 0.016 (4) Å. The H atom of the amino group is involved in an intramolecular N–H···O hydrogen bond of 2.685 (5) Å, thus keeping part of the molecule

**Related literature.** In the 1:2 complex of 18-crown-6 with guanidinium nitrate (Bandy, Truter, Wingfield & Lamb, 1981) each guanidinium cation interacts with one crown molecule and one nitrate anion. Larger macrocycles are able to encapsulate the guanidinium cation completely, as shown for 27- and 30-membered benzo- (de Boer, Uiterwijk, Geevers, Harkema & Reinhoudt, 1983) and 2,6-pyrido-crown ethers (Uiterwijk *et al.*, 1986).

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planar. The bond lengths and angles agree with expected values.

**Experimental.** Single crystals grown from ethanol solution of a mixture of 3-aminoindazole and di-*tert*-butyl fumarate. Density measured by flotation in chlorobenzene/CCl<sub>4</sub>; transparent plates, 0.20 × 0.10 × 0.05 mm; Enraf–Nonius CAD-4 diffractometer, Mo *K*α radiation (graphite monochromator), lattice parameters from 25 reflexions (6 < θ < 10°); ω/2θ scans, variable scan rate, max. scan time 60 s,