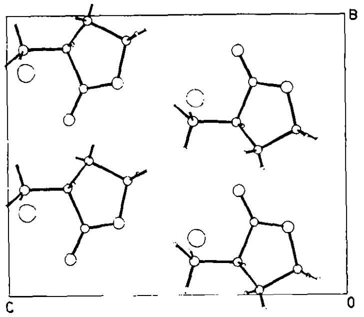

Fig. 2. Projection of the structure on (100).

151·7 (2)°; N···Br = 3·32 (1), H(6)···Br = 2·39 (10) Å, N–H(6)···Br = 164·0 (1)°. Other significant contacts are listed in Table 4 and the packing of the molecules is represented in Fig. 2.

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A 2:1 Complex of 2,4-Dinitroaniline and 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)

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Abstract. $2C_6H_5N_3O_4.C_{12}H_{24}O_6$, M_r = 630·57, monoclinic, $C2/c$, a = 14·609 (6), b = 10·843 (4), c = 18·951 (8) Å, β = 99·34 (9)°, Z = 4, d_c = 1·414 Mg m^{-3}, μ(Mo $K\alpha$) = 0·110 mm^{-1}, R = 0·074, R_w = 0·057 for 1360 independent data. The two 2,4-dinitroaniline molecules, related by a centre of inversion, are arranged perpendicularly 'above' and 'below' the plane formed by the six O atoms of the crown ether. They are linked to the latter by a system of bifurcated N–H···O bridges in which each O atom of the crown and additionally one O atom of each *o*-nitro group receives one hydrogen bond from the NH_2 groups. The conformation of the macrocyclic ligand differs from the approximate D_{3d} symmetry normally found.

Introduction. In addition to their well-known ability for ligating alkali- and alkaline-earth-metal ions, annular and linear oligoethers reveal some tendency towards forming crystalline host–guest complexes with hydrogen-bond donors such as malononitrile (Kaufmann, Knöchel, Kopf, Oehler & Rudolph, 1977), dimethyl acetylenedicarboxylate (Goldberg, 1975), thiourea (Suh & Saenger, 1978; Weber & Saenger, 1980), water (Goldberg, 1978; Bombieri, de Paoli & Immirzi, 1978; Weber & Sheldrick, 1980), benzenesulphonamide (Knöchel, Kopf, Oehler & Rudolph, 1978*a*) and (2,4-dinitrophenyl)hydrazine (Hilgenfeld & Saenger, 1981). A comparison of the last structure with the present one seemed interesting.

Yellow irregular blocks of the adduct were crystallized from ethyl acetate. Systematic absences indicated the space group Cc or $C2/c$; the latter was confirmed

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by the statistical distribution of E values and structure refinement. A crystal of approximate size 0·2 × 0·2 × 0·2 mm was used for the data collection on an automated four-circle diffractometer with monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Lp corrections were applied. 2049 unique reflexions were measured in the range $6 \leq 2\theta \leq 46°$ by a profile-fitting procedure (Clegg, 1981); 1363 data with $F > 3\sigma(F)$ were considered observed. Cell dimensions were obtained by least-squares analysis from angle measurements of 28 strong reflexions ($20 \leq 2\theta \leq 25°$).

The structure was initially solved in Cc by multisolution methods, followed by a new kind of tangent recycling involving rejection of chemically improbable peaks, and a difference Fourier synthesis. After anisotropic refinement of the non-H atoms, all H atoms could be located from difference maps. Those bonded to the N atom were given fixed common U values of 0·08 Å^2, and N—H vectors were kept constant. The remaining H atoms were assigned isotropic thermal parameters 1·2 times the U values of attached C atoms and their positions were recalculated according to stereochemical considerations (C—H = 0·96 Å, H—C—H = 109·5°, aromatic H on external bisector). In further refinement a riding model was employed.

Omission of three low-angle reflexions and application of an empirical extinction correction [$F_c^* = F_c(1 - xF_c^2/\sin\theta)$ with x = 4·6 (6) × 10^{-8}] led to final R = 0·074 and $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}F_o$ = 0·057. The weighting scheme $w^{-1} = \sigma^2(F_o) + 0{\cdot}00015F_o^2$ gave mean values of $w(|F_o| - |F_c|)^2$ virtually independent of $\sin\theta$ or $|F_o|$.

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U*
O(1)	1491 (2)	5984 (2)	977 (1)	54 (1)
C(2)	2015 (3)	6132 (4)	427 (2)	57 (2)
C(3)	2341 (3)	4930 (4)	209 (3)	76 (2)
O(4)	1580 (2)	4252 (3)	−165 (2)	75 (1)
C(5)	1810 (3)	3628 (4)	−754 (2)	57 (2)
C(6)	994 (3)	2913 (4)	−1117 (2)	59 (2)
O(7)	297 (2)	3731 (2)	−1439 (1)	51 (1)
C(8)	−541 (3)	3121 (4)	−1728 (2)	63 (2)
C(9)	−1150 (3)	2873 (3)	−1183 (2)	62 (2)
C(10)	270 (3)	7100 (3)	−1290 (2)	46 (2)
C(11)	198 (3)	8398 (3)	−1246 (2)	43 (2)
C(12)	703 (3)	9170 (4)	−1610 (2)	45 (2)
C(13)	1295 (3)	8708 (4)	−2024 (2)	48 (2)
C(14)	1388 (3)	7428 (4)	−2096 (2)	54 (2)
C(15)	891 (3)	6665 (4)	−1735 (2)	56 (2)
N(16)	−193 (2)	6284 (3)	−964 (2)	58 (2)
1H(16)	−38 (2)	5351 (3)	−1022 (2)	80
2H(16)	−550 (2)	6548 (3)	−479 (2)	80
N(17)	−429 (2)	8967 (3)	−829 (2)	58 (2)
O(18)	−853 (2)	8316 (3)	−469 (2)	73 (1)
O(19)	−514 (2)	10089 (3)	−851 (2)	100 (2)
N(20)	1826 (3)	9542 (3)	−2399 (2)	70 (2)
O(21)	1746 (3)	10649 (3)	−2315 (2)	101 (2)
O(22)	2348 (3)	9094 (3)	−2770 (2)	100 (2)

* Equivalent isotropic U except for H; $U_{eq} = \frac{1}{3}$ (trace of orthogonalized U_{ij} matrix).

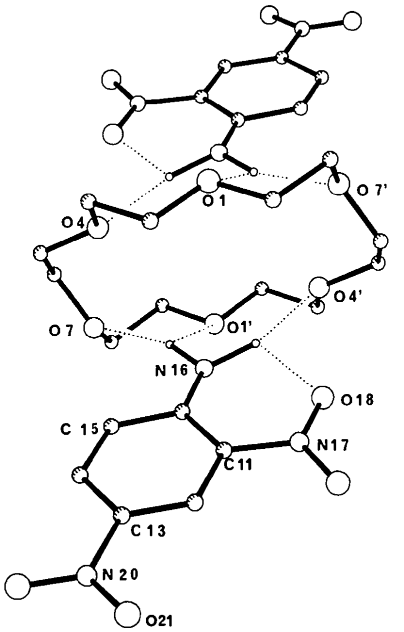

Fig. 1. A perspective view of the adduct. Primed atoms are related to the corresponding unprimed ones by inversion at the centre of 18-crown-6 (0,½,0). Radii are arbitrary.

Table 2. *Bond lengths* (Å)

C(2)–O(1)	1·400 (4)	C(2)–C(3)	1·469 (6)
C(3)–O(4)	1·422 (6)	C(5)–O(4)	1·391 (7)
C(5)–C(6)	1·492 (7)	C(6)–O(7)	1·412 (6)
C(8)–O(7)	1·421 (6)	C(8)–C(9)	1·493 (8)
C(9)–O(1)′	1·414 (6)	C(10)–C(11)	1·416 (6)
C(10)–C(15)	1·416 (8)	C(10)–N(16)	1·326 (7)
C(11)–C(12)	1·373 (7)	C(11)–N(17)	1·443 (7)
C(12)–C(13)	1·355 (7)	C(13)–C(14)	1·404 (7)
C(13)–N(20)	1·450 (7)	C(14)–C(15)	1·357 (7)
N(17)–O(18)	1·218 (6)	N(17)–O(19)	1·223 (5)
N(20)–O(21)	1·219 (6)	N(20)–O(22)	1·219 (7)
N(16)–1H(16)	1·046	N(16)–2H(16)	1·163

Table 3. *Bond angles* (°)

C(2)–O(1)–C(9)′	111·4 (4)	O(1)–C(2)–C(3)	110·4 (3)
C(2)–C(3)–O(4)	109·7 (4)	C(3)–O(4)–C(5)	112·4 (4)
O(4)–C(5)–C(6)	110·1 (5)	C(5)–C(6)–O(7)	109·8 (4)
C(6)–O(7)–C(8)	113·0 (4)	O(7)–C(8)–C(9)	113·0 (5)
C(8)–C(9)–O(1)′	108·0 (4)	C(11)–C(10)–C(15)	115·3 (5)
C(11)–C(10)–N(16)	126·0 (5)	C(15)–C(10)–N(16)	118·7 (5)
C(10)–C(11)–C(12)	121·7 (5)	C(10)–C(11)–N(17)	121·2 (5)
C(12)–C(11)–N(17)	117·1 (4)	C(11)–C(12)–C(13)	120·7 (5)
C(12)–C(13)–C(14)	120·2 (5)	C(12)–C(13)–N(20)	119·7 (5)
C(14)–C(13)–N(20)	120·1 (5)	C(13)–C(14)–C(15)	119·1 (5)
C(10)–C(15)–C(14)	123·0 (5)	C(11)–N(17)–O(18)	119·0 (4)
C(11)–N(17)–O(19)	118·5 (5)	O(18)–N(17)–O(19)	122·5 (5)
C(13)–N(20)–O(21)	118·7 (5)	C(13)–N(20)–O(22)	118·0 (5)
O(21)–N(20)–O(22)	123·3 (5)	1H(16)–N(16)–2H(16)	117·0

Table 1 lists the coordinates of all refined atoms, with derived bond lengths and angles in Tables 2 and 3;

H atoms of the NH_2 group are also included.* A view of the complex and the numbering scheme is presented in Fig. 1.

Discussion. 18-Crown-6 normally adopts a conformation of approximate D_{3d} symmetry both in cationic complexes (*e.g.* Dunitz, Dobler, Seiler & Phizackerley, 1974; Nagano, 1979) and when hydrogen bonding to guest species (Nagano, Kobayashi & Sasaki, 1978; Goldberg, 1975; Kaufmann *et al.*, 1977; Hilgenfeld & Saenger, 1981) including cation-coordinated water (Knöchel, Kopf, Oehler & Rudolph, 1978*b*). With dihydrated uranyl nitrate (Bombieri, de Paoli & Immirzi, 1978) or benzenesulphonamide (Knöchel *et al.*, 1978*a*), however, this symmetry with exclusively *anti–gauche–anti* units of alternating signs is broken in favour of an elongated conformation $g^+g^+aag^-aag^-ag^-g^-aag^+aag^+a$ which is related to that of the uncomplexed ether (Maverick, Seiler, Schweizer & Dunitz, 1980). The same pattern is found in the present structure (Fig. 2) if C(2)–C(3)–O(4)–C(5) *ca* 140° (Table 4)* is considered to be (strongly distorted) *anti*. However, the highly anisotropic vibrations of C(3) and O(4) may reflect partial disorder and thus make the value of this angle unreliable.

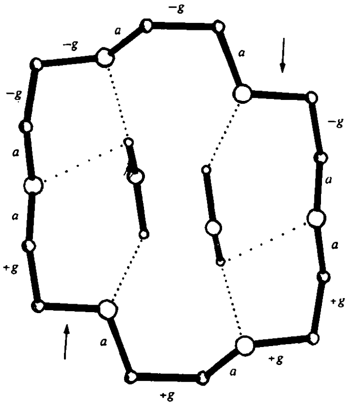

Fig. 2. The conformation of 18-crown-6 (*a* = *anti*, ±*g* = ±*gauche*) and the system of intermolecular hydrogen bridges viewed in a direction normal to the best plane of the six O atoms. Arrows indicate torsion angles *ca* ± 140°.

Table 4. *Torsion angles* (°) *for the macrocyclic ligand*

C(9)′–O(1)–C(2)–C(3)	−178·5 (4)	O(1)–C(2)–C(3)–O(4)	71·3 (5)
C(2)–C(3)–O(4)–C(5)	139·3 (4)	C(3)–O(4)–C(5)–C(6)	178·8 (4)
O(4)–C(5)–C(6)–O(7)	68·3 (6)	C(5)–C(6)–O(7)–C(8)	−173·5 (5)
C(6)–O(7)–C(8)–C(9)	83·5 (5)	O(7)–C(8)–C(9)–O(1)′	69·0 (5)
C(8)–C(9)–O(1)′–C(2)′	−175·6 (5)		

Despite conformational irregularities, the O atoms of the macrocycle form a fairly regular hexagon [O(1)···O(4) = 2·884 (6), O(4)···O(7) = 2·861 (6), O(7)···O(1)′ = 2·904 (6) Å] and are located alternately about 0·25 Å 'above' and 'below' their mean plane, similar to those structures with D_{3d} symmetry (Dunitz *et al.*, 1974; Goldberg, 1975; Nagano *et al.*, 1978). Bond distances and angles follow the general trend in oligoethers, *i.e.* C–C distances (average 1·485 Å) appear somewhat shortened while C–O distances (average 1·410 Å) are more or less 'normal', C–O–C angles are slightly widened (average 112·3°) and O–C–C are almost tetrahedral, averaging 110·2°.

The two guest molecules, related by inversion at the centre of 18-crown-6, are located almost perpendicular to the hexagon of O atoms on either side of the ligand. Dihedral angles between the phenyl plane and the *o*- and *p*-nitro groups [4·8 (5) and 1·3 (4)° respectively] correspond to short C–N distances of 1·443 (7) and 1·450 (7) Å (Kawai, Kashino & Haisa, 1976). The less accurately determined rotation of the amino group [8·3 (7)°] is smaller than in *o*-nitroaniline (Dhaneshwar, Tavale & Pant, 1978); the short C(10)–N(16) bond [1·326 (7) Å] and lengthened adjacent C–C bonds in the ring (1·416 Å) fit the correlation reported for primary aromatic amines (Holden, Dickinson & Bock, 1972). Thus the approximate coplanarity and, especially, the distribution of bond distances in 2,4-dinitroaniline indicate considerable quinonoid contributions to the overall resonance state of the molecule.

The resulting increased acidity of the amino group probably facilitates the formation of bifurcated hydrogen bridges (Table 5) by which host and guests are linked. The strengths of these intermolecular hydrogen bonds seem to be related to N–H···O angles: the shortest contact 1H(16)···O(7) = 2·019 (7) Å corresponds to an angle N(16)–1H(16)···O(7) of 162·4 (5)° and the weakness of the 1H(16)···O(1)′ interaction [2·583 (6) Å] is reflected in an N(16)–1H(16)···O(1)′ angle of only 110·1 (4)°. Possibly in order to allow hydrogen bonds to all O atoms of the crown, the atoms of the intramolecular chelate ring completed by 2H(16)···O(18) deviate more from coplanarity (±0·12 Å) than is observed in *o*-nitroaniline (Dhaneshwar *et al.*, 1978) and in the 1:2 adduct of 18-crown-6 and (2,4-dinitrophenyl)hydrazine (Hilgenfeld & Saenger, 1981).

Table 5. *Hydrogen-bridge distances* (Å) *and angles* (°)

N(16)···O(1)′	3·103 (6)	1H(16)···O(1)′	2·583 (6)
N(16)···O(4)′	3·230 (7)	2H(16)···O(4)′	2·260 (7)
N(16)···O(7)	3·032 (7)	1H(16)···O(7)	2·019 (7)
N(16)···O(18)	2·638 (7)	2H(16)···O(18)	1·969 (7)
N(16)–1H(16)···O(1)′	110·1 (4)	N(16)–1H(16)···O(7)	162·4 (5)
N(16)–2H(16)···O(4)′	139·1 (5)	N(16)–2H(16)···O(18)	112·2 (5)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36175 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

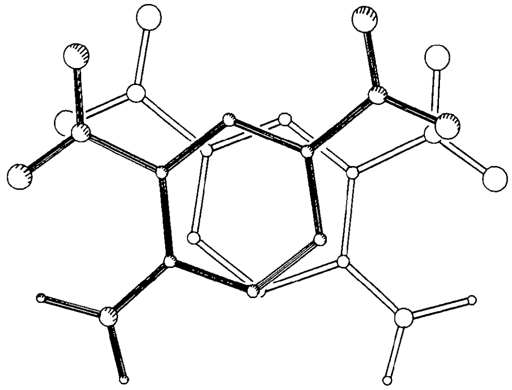

Fig. 3. Partial overlap (*ca* 75%) of aromatic nuclei 3·61 (7) Å apart, related by the twofold rotation axis at $x = 0$, $z = -\frac{1}{4}$.

Comparing the latter structure to the current one, many analogies can be detected such as the overall arrangement of the molecules (including the inversion centre), interactions with all O atoms, bifurcation of hydrogen bridges and stacking in the lattice (Fig. 3). The assumed correlation between acidity and crystal stability (Hilgenfeld & Saenger, 1981) is supported by the present structure which involves the more acidic 2,4-dinitroaniline, and by the fact that only poor crystals (and data) of the 1:2 adduct of 18-crown-6 and the less acidic *p*-nitroaniline (Weber, unpublished) could be obtained.

Due to the steric requirements of 2,4-dinitrophenylhydrazine, the system of hydrogen bridges in its complex with 18-crown-6 is quite intricate; the macrocycle, however, stays relatively free of conformational strain and keeps its approximate D_{3d} symmetry. In contrast, the rather 'simple' system of hydrogen bridges in the 2,4-dinitroaniline complex forces the ligand into an unusual strained conformation. This is further evidence for the structural versatility of a cyclic oligoether.

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5-Nitro-L-histidine Monohydrate

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Abstract. $C_6H_8N_4O_4.H_2O$, orthorhombic, $P2_12_12_1$, $a = 12·519\ (4)$, $b = 10·757\ (3)$, $c = 6·590\ (1)$ Å, $V = 887·5\ (7)$ Å^3, $Z = 4$, $D_c = 1·63$ Mg m^{-3}. The structure was solved with *MULTAN* and refined by full-matrix least squares. The final R is 0·045 for 1127 observed reflections. The torsion angles are similar to those obtained in L-histidine. The nitro substituent modifies the bond distances in the imidazolyl ring.

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