dihedral angles between the plane through C(1), C(2), C(3) of the five-membered ring and the phenyl rings *A*, *B* and *C* are 44·7 (4), 43·8 (5), 98·4 (5)° respectively. The benzene molecules lie on centres of symmetry and stack in channels parallel to **a**.

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A 1:2 Host–Guest Complex Between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and *N*,*N*′-Diformohydrazide, $C_{12}H_{24}O_6.2C_2H_4N_2O_2$

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Abstract. $M_r = 440{\cdot}5$, monoclinic, $P2_1/n$, $a = 14{\cdot}176\,(2)$, $b = 9{\cdot}968\,(2)$, $c = 8{\cdot}121\,(1)$ Å, $\beta = 103{\cdot}34\,(1)°$, $V = 1116{\cdot}6\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}310$, $D_m = 1{\cdot}29\,(1)$ Mg m^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}94$ mm^{-1}, $F(000) = 472$, $T = 293$ K. Final $R = 0{\cdot}044$ for 1218 unique observed reflections. The 18-crown-6 molecule lies on an inversion center and its conformation deviates only slightly from D_{3d} symmetry. The conformation of the guest *N*,*N*′-diformohydrazide approximates C_2 symmetry with a torsion angle of 105·4 (4)° around the N—N bond. Two inversion-related crown ether O atoms are each hydrogen-bonded to an N—H group of the guest molecule. Guest molecules are linked by two identical N—H···O=C hydrogen bonds which are related by another inversion center.

Introduction. Although complexes between uncharged organic molecules play a fundamental role in biochemical processes, it is an area that remains relatively unexplored. Many data have been gathered on interactions involving hydrogen bonding; however, it is still difficult to suggest specific hosts (receptors) for the complexation of neutral (uncharged) guest molecules. The importance of 'acidic' methyl and methylene groups in stabilizing complexes between neutral molecules has not been appreciated (Goldberg, 1975; Bandy, Truter & Vögtle, 1981; Kaufmann, Knochel, Kopf, Oehler & Rudolph, 1977; Watson, Galloy, Grossie, Vögtle & Müller, 1983). While such interactions are weak, they lead to well-ordered crystalline solids and may be of importance in orienting and directing substrate molecules at active sites. When the guest molecule contains only one hydrogen capable of interacting with an 18-crown-6 host, usually a molecule of water is incorporated to form a ternary complex (Grossie, Watson, Vögtle & Müller, 1982; Watson *et al.*, 1983) or a complex of unusual stoichiometry is formed. In order to provide additional data for the development of theories for predicting structures of hosts for specific guests, we have examined the title compound.

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Experimental. Reaction of 18-crown-6 and *N,N'*-diformohydrazide in a 1:2 molar ratio in ethanol yielded colorless needles of title complex (Vögtle & Müller, 1980), 0·25 × 0·25 × 0·42 mm. D_m measured by flotation in CCl_4/cyclohexane. Syntex $P2_1$ diffractometer. Lattice parameters from least-squares refinement of computer data for 15 reflections ($11\cdot0 < 2\theta < 30\cdot0°$). $(\sin\theta/\lambda)_{\max} = 0\cdot546$ Å^{-1}, range of *hkl*: 0–14, 0–10, −8–8, θ:2θ scan mode, scan speed 3·91–29·30° min^{-1}, background scan time/peak scan time 1·0. One standard reflection (020) showed no systematic variation. Lp corrections but no correction for absorption. 1811 reflections measured, 109 systematically absent, 1505 unique, 1218 observed with $I > 3\sigma(I)$. All non-H atoms located in an *E* map phased by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Most H atoms revealed in difference syntheses. Positions of the two amide H atoms allowed to refine but remaining H atoms included in a riding model at idealized positions (C—H = 1·08 Å) with fixed isotropic temperature factors (0·059–0·070 Å^2) equal to those of their parent atoms. Anisotropic temperature factors assigned to all non-H atoms in final cycles of refinement. Quantity minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$. 142 parameters refined. Final $R = 0\cdot044$, $R_w = 0\cdot058$, $S = 2\cdot788$. $(\Delta/\sigma)_{av} = 0\cdot01$, $(\Delta/\sigma)_{\max} = 0\cdot06$. Highest peak in difference map 0·17 e Å^{-3}. All calculations performed with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Table 1 lists final atomic coordinates and isotropic thermal parameters. Bond lengths, bond angles and hydrogen-bond data are listed in Table 2.*

The structure is illustrated in Fig. 1 which includes the atomic numbering. The space group requires the 18-crown-6 molecule to lie on an inversion center (chosen at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). Two *N,N'*-diformohydrazide guest molecules, related by the same center of symmetry, are linked to the crown ether *via* one N—H···O hydrogen bond each. The structure is unusual in that only two O atoms of the crown ether are involved in hydrogen bonding (Watson *et al.*, 1983). Hydrogen bonding between guest molecules provides additional stability and steric blocking of the remaining crown ether sites. As previously reported (Grossie *et al.*, 1982), the macrocyclic host has a conformation approaching D_{3d} symmetry with the six O atoms alternately about 0·23 Å above and below their mean plane. Average parameters with mean deviations are: C—C 1·495 (3), C—O 1·419 (5), O···O 2·85 (3) Å, C—O—C 112·1 (5), O—C—C 108·9 (4)°. The magnitudes of O—C—C—O and C—C—O—C torsion angles are in the ranges 67·2 (3) to 72·2 (3)° and 176·7 (2) to 179·8 (3)° respectively.

The structure and electronic properties of *N,N'*-diformohydrazide have been the subject of several recent theoretical and experimental studies (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1982; Hope & Ottersen, 1979; Eisenstein, 1979; Hope & Ottersen, 1978; Tanaka, 1978). The molecule adopts a centrosymmetric *cis–trans* conformation in the crystal. Jeffrey *et al.* have shown by *ab initio* MO methods that this conformer is the most stable of the various possible planar conformers. When they released the constraint of planarity, however, they found a conformer with molecular symmetry C_2 and C—N—N—C torsion angle of 84·5° to be the most stable for the isolated molecule.

In the title complex, the *N,N'*-diformohydrazide molecule has a pseudo-twofold axis passing through the midpoint of the N—N bond and the torsion angle C(10)—N(1)—N(2)—C(11) is 105·4 (4)°. The N—N distance, 1·399 (4) Å, compares favorably with the value of 1·386 (2) Å observed in *N,N'*-dimethyl-*N,N'*-diformohydrazide which also displays a *gauche* conformation (Ottersen, 1978). For N—N in *N,N'*-diformohydrazide, accurate low-temperature X-ray and neutron diffraction studies yielded respectively 1·3797 (2) (Hope & Ottersen, 1978) and 1·3808 (4) Å (1·387 Å after thermal-motion correction) (Jeffrey *et al.*, 1982).

Each —NHCHO moiety is fairly planar [dihedral angles N(2)—N(1)—C(10)—O(10) 3·3 (5), N(1)—N(2)—C(11)—O(11) 2·1 (4)°] and the N atoms maintain essentially trigonal geometry, as observed in the *N,N'*-dimethyl derivative. Pyramidizations at N(1) and N(2) are approximately 4 and 0° respectively. Slight differences in the C—N and C=O distances reflect different extents of hydrogen-bond participation by the two formamide fragments.

Each guest molecule forms three N—H···O hydrogen bonds, two of which are crystallographically distinct. The N(1)—H(1)···O(7) hydrogen bond binds the host and guest molecules while the latter are linked to one another by two identical N—H···O=C hydrogen bonds related by the inversion center at $\frac{1}{2}, \frac{1}{2}, 0$ (Table 2 and Fig. 1). Although the H···O and N···O distances are normal for N—H···O=C hydrogen bonding (Donohue, 1968), the N—H donor deviates considerably from the plane of the carbonyl system. Hydrogen bonding thus links host and guest molecules in infinite chains along the *z* direction, two guest molecules being sandwiched between translated crown ether molecules. Atom O(11) does not participate in hydrogen bonding but makes contacts just less than 2·6 Å with H atoms of the crown ether. Atom H(10) has similar contact distances to atoms O(4^{i}) and O(7^{i}). Details are not reported as only

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* Lists of H-atom coordinates, anisotropic thermal parameters, dihedral angles, equations of least-squares planes and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38876 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

weak interactions are implied and the H atoms involved are in idealized positions. The relevant crown ether O-atom sites do, however, appear to be sterically blocked by these C—H···O interactions. An interesting comparison is provided by the structure of the complex 18-crown-6.(2,4-dinitrophenylhydrazine)$_2$ (Hilgenfeld & Saenger, 1981). In this centrosymmetric complex, both of the N—H groups of two guest molecules form N—H···O hydrogen bonds with the host. Moreover, since some of these interactions are bifurcated, all of the ether O atoms act as acceptors. In contrast, the presence of —CHO substituents on the hydrazine in the title complex leads to a structure in which host–guest and guest–guest binding have comparable strength.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*/U_{iso}(Å^2)
O(1)	5099 (1)	2509 (2)	3587 (2)	60 (1)
C(2)	6058 (2)	2001 (3)	3955 (4)	73 (2)
C(3)	6725 (2)	3018 (3)	3476 (4)	72 (2)
O(4)	6851 (1)	4090 (2)	4647 (2)	64 (1)
C(5)	7464 (2)	5105 (3)	4271 (4)	70 (2)
C(6)	7514 (2)	6217 (3)	5526 (4)	71 (2)
O(7)	6591 (1)	6836 (2)	5255 (2)	57 (1)
C(8)	6560 (2)	7871 (3)	6460 (3)	63 (2)
C(9)	5567 (2)	8458 (3)	6065 (3)	63 (2)
N(1)	5050 (2)	6168 (3)	2438 (3)	69 (2)
C(10)	4275 (2)	5403 (3)	2247 (4)	62 (2)
O(10)	3760 (2)	5067 (2)	885 (3)	74 (1)
N(2)	5339 (2)	6741 (3)	1060 (3)	75 (2)
C(11)	5208 (2)	8045 (4)	708 (4)	71 (2)
O(11)	4869 (2)	8831 (3)	1529 (3)	92 (2)
H(1)	545 (2)	632 (3)	339 (4)	60
H(2)	561 (2)	616 (3)	47 (3)	62

* $U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^* \times \cos\beta + 2U_{23}bcb^*c^* \cos\alpha + 2U_{12}a^*b^*ab \cos\gamma]$.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond data with e.s.d.'s in parentheses*

O(1)—C(2)	1·417 (3)	N(1)—N(2)	1·399 (4)
O(1)—C(9^i)	1·423 (4)	N(1)—C(10)	1·317 (4)
C(2)—C(3)	1·498 (4)	N(2)—C(11)	1·335 (5)
C(3)—O(4)	1·414 (4)	C(10)—O(10)	1·223 (4)
O(4)—C(5)	1·412 (4)	C(11)—O(11)	1·199 (5)
C(5)—C(6)	1·496 (4)	N(1)—H(1)	0·86 (3)
C(6)—O(7)	1·417 (3)	N(2)—H(2)	0·89 (3)
O(7)—C(8)	1·430 (3)		
C(8)—C(9)	1·490 (4)		
C(9^i)—O(1)—C(2)	111·4 (2)	N(2)—N(1)—C(10)	122·2 (2)
O(1)—C(2)—C(3)	109·6 (2)	N(1)—N(2)—C(11)	121·1 (3)
C(2)—C(3)—O(4)	109·0 (3)	N(1)—C(10)—O(10)	124·9 (3)
C(3)—O(4)—C(5)	112·6 (2)	N(2)—C(11)—O(11)	124·8 (3)
O(4)—C(5)—C(6)	108·6 (3)	H(1)—N(1)—C(10)	125 (2)
C(5)—C(6)—O(7)	108·7 (2)	H(1)—N(1)—N(2)	113 (2)
C(6)—O(7)—C(8)	112·4 (2)	H(2)—N(2)—C(11)	125 (2)
O(7)—C(8)—C(9)	108·2 (2)	H(2)—N(2)—N(1)	114 (2)
C(8)—C(9)—O(1^i)	109·2 (2)		
N(1)···O(7)	2·854 (3) Å	N(1)—H(1)···O(7)	166 (2)°
H(1)···O(7)	2·01 (3)		
N(2)···O(10^{ii})	2·882 (4) Å	N(2)—H(2)···O(10^{ii})	177 (2)°
H(2)···O(10^{ii})	1·99 (3)	C(10)—O(10)···H(2^{ii})	115 (2)

Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$.

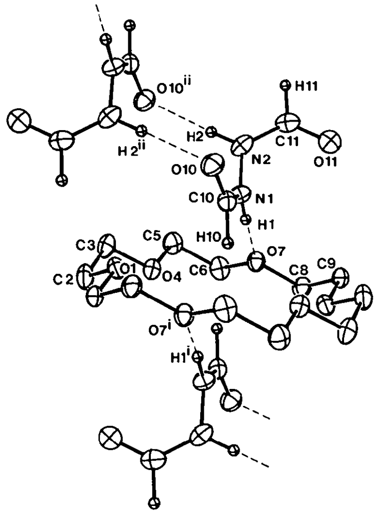

Fig. 1. *ORTEP* plot (Johnson, 1971) showing thermal ellipsoids at the 20% probability level. Inversion centers are at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (lower) and $\frac{1}{2}, \frac{1}{2}, 0$ (upper) and hydrogen bonds are indicated by dashed lines. H atoms of the crown ether have been omitted for clarity.

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