Molecules of alcohol (I) dimerize about a center of symmetry with rather weak hydrogen bonds, O(11)···O(12) 2·938 (3) Å. All other intermolecular separations for (I) and all intermolecular separations for (II) appear to be normal van der Waals contacts.

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A 1:2 Complex between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and 2-(2-Benzimidazolyl)guanidine, $C_{12}H_{24}O_6.2C_8H_9N_5$

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Abstract. $M_r = 614{\cdot}7$, monoclinic, $C2/c$, $a = 20{\cdot}894$ (4), $b = 8{\cdot}399$ (1), $c = 18{\cdot}330$ (3) Å, $\beta = 93{\cdot}09$ (2)°, $V = 3212$ (1) Å^3, $D_x = 1{\cdot}271$ Mg m^{-3}, $Z = 4$, $F(000) = 1312$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu } K\alpha) = 0{\cdot}77$ mm^{-1}, $T = 293$ K, $R = 0{\cdot}049$ for 1462 independent reflexions. The 18-crown-6 molecule lies at an inversion center and adopts the D_{3d} conformation. Two guest 2-(2-benzimidazolyl)guanidine molecules, related by the same center of symmetry, bind to the crown ether *via* (guanidine)N—H···O hydrogen bonds. Additional stabilization is provided by intramolecular N—H···N, as well as intermolecular base-pairing N—H···N hydrogen bonding involving guest molecules. The structure is compared with that of the known isomorphous analogue, (1,10-diaza-18-crown-6).[2-(2-benzimidazolyl)guanidine]$_2$.

Introduction. Molecular-mechanics calculations on 18-crown-6 (Bovill, Chadwick & Sutherland, 1980) indicate that the D_{3d} conformation lies 32·8 kJ mol^{-1} above the lowest-energy conformation. The lowest-energy conformation corresponds to that adopted in the crystalline state (Dunitz & Seiler, 1974). The D_{3d} conformation would be the lowest-energy conformation if it were not for the unfavorable dipolar interactions between the three O atoms on each face. The D_{3d} conformation becomes favored when the dipolar interactions are minimized by coordination to electron acceptors. Trigonal acceptors (—XH_3) or acceptors bridging alternate ether O atoms stabilize the D_{3d} conformation. Unfavorable or widely separated acceptor sites can lead to the stabilization of alternate conformations.

The replacement of ether O atoms by —NH— groups provides sites which can act as either electron or proton donors. In the 1:4 complex of 1,10-diaza-18-crown-6 with thiourea the aza-group H atom bonds intramolecularly to an adjacent ether O which aids in the stabilization of a biangular conformation (Weber, 1982). In the 1:2 complex of 1,10-diaza-18-crown-6 with 2-(2-benzimidazolyl)guanidine the crown adopts a D_{3d} conformation (Watson, Galloy, Grossie, Vögtle &

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Müller, 1984). Although there was no specific evidence for an intermolecular hydrogen bond, the geometry was such that a hydrogen bond might exist between the aza H atom and a guest N atom. The data quality did not permit the location of these H atoms. It was of interest to assess whether replacement of two host —NH— functional groups in the diaza-18-crown-6 complex by two —O— functions in 18-crown-6 might lead to a difference in host conformation and/or host–guest binding geometry.

Geometrical parameters for the guanidine moiety in the diaza-18-crown-6 complex were consistent with the amino tautomeric form. However, since host–guest binding involves this group, and since H atoms could not be located with confidence, a further aim of this analysis was to confirm the tautomeric assignment for the guest in complexes of this type.

Experimental. D_m not determined. Elongated prism 0·33 × 0·18 × 0·15 mm. Syntex $P2_1$ diffractometer. Lattice parameters by least-squares refinement of angular data for 15 reflections. Space group *Cc* or *C*2/*c* indicated from systematic absences $h + k = 2n + 1$ for *hkl*, $l = 2n + 1$ for *h*0*l*. 2373 independent reflections, $(\sin\theta/\lambda)_{\max} = 0{\cdot}546$ Å^{-1}, *hkl* range: 22,9,±19, θ:2θ scan technique, Cu $K\alpha$ radiation, variable scan speed; only 1462 reflections had $I > 3\sigma(I)$ owing to the small crystal size. Intensity of a check reflection showed no systematic variation. Lorentz–polarization corrections; absorption ignored ($\mu R_{\max} = 0{\cdot}25$). Intensity statistics indicated space group *C*2/*c*. The direct-methods program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) yielded the positions of all non-hydrogen atoms. Idealized positions (C—H 1·08 Å) were calculated for the H atoms of the crown ether and phenyl ring and difference Fourier syntheses were carefully searched for the remaining guest H atoms. Peaks associated with N(10) and N(11) were found in approximately trigonal positions whereas no peak was found near N(13). H(22) was also located. In the final cycles of least-squares refinement with program *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), anisotropic thermal parameters were assigned to the non-hydrogen atoms and the positions of the five H—(N) atoms were allowed to refine. All H atoms were given fixed isotropic thermal parameters equal to those of their parent atoms (0·044–0·095 Å^2). $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$. Refinement yielded $R = 0{\cdot}049$, $R_w = 0{\cdot}057$, $S = 2{\cdot}376$, $(\Delta/\sigma)_{\max} = 0{\cdot}23$, and $(\Delta/\sigma)_{\text{avg}} = 0{\cdot}07$. No chemical significance could be placed on the largest peak (0·37 e Å^{-3}) in the final difference synthesis. Atomic scattering factors for C,N,O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). No correction for secondary extinction.

Discussion. Table 1 lists fractional atomic coordinates for the non-hydrogen atoms and equivalent isotropic thermal parameters.* Pertinent bond lengths and angles for the guest 2-(2-benzimidazolyl)guanidine are listed in Table 2. Hydrogen-bond data appear in Table 3.

The title complex (Fig. 1) and (1,10-diaza-18-crown-6).[2-(2-benzimidazolyl)guanidine]$_2$ are isomorphous and isoelectronic. The two centrosymmetrically related host N—H groups of the latter complex are replaced by atoms O(4), O(4^i) here. Owing to the close correspondence between the two structures, only a brief description is reported, but details of the hydrogen-bonding scheme (not mentioned previously) are discussed.

The 18-crown-6 host is located on an inversion center and adopts the D_{3d} conformation with the six O atoms alternately about 0·19 Å above and below their mean plane. This deviation is closer to that observed for the O and N atoms in the 1,10-diaza-18-crown-6 analogue (0·18 Å) than to that usually found for the O atoms in complexes of 18-crown-6 (0·23–0·25 Å) (Caira, Watson, Vögtle & Müller, 1984*a*,*b*; Watson, Galloy, Grossie, Vögtle & Müller, 1984), which implies that the finer conformational features of the host are guest-dependent. (Uncertainties in the atomic positions for these complexes at the 5% probability level generally do not exceed 0·02 Å.) Average parameters for the crown ether with mean deviations are: C—C 1·49 (1), C—O 1·41 (1), O···O 2·82 (5) Å, C—O—C 113 (1), O—C—C 110 (2)°. As expected, the C(3)—O(4), C(5)—O(4) distances [1·415 (6), 1·383 (7) Å] are shorter than the host C—N distances [1·477 (6), 1·435 (7) Å] in the analogous diaza-18-crown-6 complex.

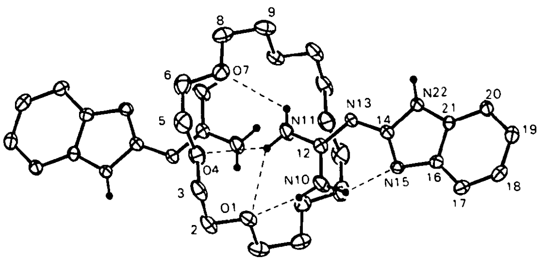

Fig. 1. *ORTEP* plot (Johnson, 1971) of the title complex with thermal ellipsoids drawn at the 20% probability level. Dashed lines represent the unique host–guest O···H—N and intramolecular guest N—H···N hydrogen bonds. For clarity, only the H—(N) atoms are included. Atoms labeled with numerals only are C atoms.

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* Lists of bond lengths, valence angles, torsion angles, equations of least-squares planes, anisotropic thermal parameters, H-atom coordinates and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39241 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	y	z	U_{eq} or U_{iso} (Å^2)
O(1)	4104 (1)	1441 (3)	−1038 (1)	74 (2)
C(2)	4407 (2)	2013 (5)	−1666 (2)	85 (3)
C(3)	4985 (3)	2940 (5)	−1420 (2)	87 (3)
O(4)	5431 (2)	1853 (3)	−1093 (1)	85 (2)
C(5)	6027 (3)	2513 (6)	−925 (3)	103 (4)
C(6)	6478 (2)	1373 (6)	−562 (3)	91 (3)
O(7)	6286 (1)	960 (3)	129 (2)	77 (2)
C(8)	6734 (2)	27 (5)	544 (3)	85 (3)
C(9)	6433 (2)	−504 (5)	1232 (2)	87 (3)
N(10)	3990 (2)	3112 (4)	459 (2)	72 (2)
N(11)	4942 (2)	1773 (5)	482 (2)	70 (2)
C(12)	4483 (2)	2460 (4)	848 (2)	52 (2)
N(13)	4554 (1)	2477 (3)	1572 (1)	50 (2)
C(14)	4105 (2)	3180 (4)	1976 (2)	46 (2)
N(15)	3577 (1)	3982 (3)	1768 (1)	49 (2)
C(16)	3324 (2)	4494 (4)	2421 (2)	48 (2)
C(17)	2794 (2)	5437 (5)	2537 (2)	62 (2)
C(18)	2657 (2)	5772 (5)	3255 (2)	68 (3)
C(19)	3036 (2)	5191 (5)	3842 (2)	66 (3)
C(20)	3576 (2)	4278 (4)	3739 (2)	59 (2)
C(21)	3709 (2)	3952 (4)	3019 (2)	47 (2)
N(22)	4201 (1)	3109 (3)	2723 (1)	50 (2)
H(10*A*)	400 (2)	293 (4)	−2 (2)	70
H(10*B*)	368 (2)	352 (4)	73 (2)	70
H(11*A*)	523 (2)	130 (4)	72 (2)	64
H(11*B*)	489 (2)	168 (4)	1 (2)	64
H(22)	455 (1)	280 (4)	293 (2)	44

Table 2. *Selected distances* (Å) *and angles* (°) *in* 2-(2-*benzimidazolyl*)*guanidine with e.s.d.'s in parentheses*

	(*a*)	(*b*)
C(12)–N(10)	1·338 (5)	1·351 (6)
C(12)–N(11)	1·331 (6)	1·350 (6)
C(12)–N(13)	1·327 (4)	1·331 (5)
N(13)–C(14)	1·361 (5)	1·358 (5)
C(14)–N(15)	1·331 (5)	1·312 (5)
C(14)–N(22)	1·374 (4)	1·381 (5)
N(10)–H(10*A*)	0·89 (3)	—
N(10)–H(10*B*)	0·90 (4)	—
N(11)–H(11*A*)	0·83 (4)	—
N(11)–H(11*B*)	0·87 (4)	—
N(22)–H(22)	0·84 (3)	—
N(10)–C(12)–N(11)	117·6 (3)	119·4 (4)
N(10)–C(12)–N(13)	124·7 (4)	123·4 (4)
N(11)–C(12)–N(13)	117·6 (3)	117·1 (4)
C(12)–N(13)–C(14)	120·4 (3)	121·2 (3)

(*a*) This work.
(*b*) (1,10-Diaza-18-crown-6). [2-(2-benzimidazolyl)guanidine]$_2$.

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

N(10)···O(1)	3·103 (4)	N(11)···O(7)	2·994 (5)
H(10*A*)···O(1)	2·27 (4)	H(11*A*)···O(7)	2·53 (4)
N(10)–H(10*A*)···O(1)	156 (3)	N(11)–H(11*A*)···O(7)	117 (3)
N(11)···O(1)	3·222 (4)	N(10)···N(15)	2·694 (4)
H(11*B*)···O(1)	2·47 (4)	H(10*B*)···N(15)	1·96 (4)
N(11)–H(11*B*)···O(1)	145 (3)	N(10)–H(10*B*)···N(15)	137 (3)
N(11)···O(4)	3·115 (5)	N(22)···N(13^{ii})	2·891 (3)
H(11*B*)···O(4)	2·37 (5)	H(22)···N(13^{ii})	2·06 (2)
N(11)–H(11*B*)···O(4)	145 (3)	N(22)–H(22)···N(13^{ii})	170 (3)

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

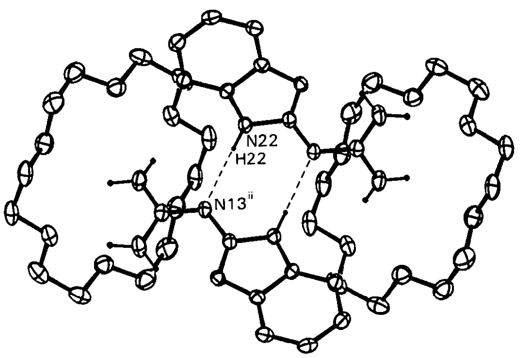

Fig. 2. (010) projection showing hydrogen bonding (dashed lines) between diad-related guest molecules.

The uniformity of the three C(12)—N distances and the angles around C(12) and N(13) in both complexes (Table 2) indicate that the guanidine group is in the amino form. This was confirmed in the present study by the successful location of the four amino H atoms. Refinement of their positions yielded essentially planar $-NH_2$ groups with H—N—H and H—N—C(12) angles (ideally 120°) in the range 113 (2)–131 (3)°.

The crystal structure is stabilized by a variety of hydrogen bonds which involve all potential donors and acceptors. Host–guest binding occurs *via* one normal, one rather weak, and one bifurcated O···H—N(guanidine) hydrogen bond (Fig. 1, Table 3) and their inversion-related equivalents. The fourth guanidine H atom is intramolecularly hydrogen bonded to N(15). In addition, crystallographic twofold axes are utilized to form guest base-pairs linked by N(22)—H(22)···N(13^{ii}) hydrogen bonds (Fig. 2). All 13 non-hydrogen atoms of the guest are coplanar (average deviation from the least-squares plane 0·03 Å, maximum 0·07 Å) and the dihedral angle between the hydrogen-bonded planes is approximately 66°. The entire structure is therefore built up from infinite chains of molecules, linked along the z direction by alternating host–guest, guest–guest hydrogen bonds.

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1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methanoanthracene†(1) (*syn*-Oxabenzosesquinorbornene), $C_{15}H_{14}O$, and Adducts with Dichlorocarbene (2), $C_{16}H_{14}Cl_2O$, and Anthranilic Acid (3), $C_{23}H_{18}N_2O_3$

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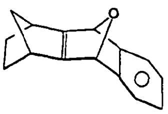
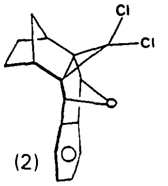
Abstract. (1): $M_r = 210{\cdot}28$, orthorhombic, $Pna2_1$, $a = 21{\cdot}552\ (7)$, $b = 6{\cdot}503\ (3)$, $c = 7{\cdot}652\ (2)$ Å, $V = 1072{\cdot}5\ (7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}302$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}86$ cm^{-1}, $F(000) = 448$, room temperature, $R = 0{\cdot}046$ for 1026 unique reflections. (2): $M_r = 293{\cdot}19$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}821\ (4)$, $b = 28{\cdot}184\ (9)$, $c = 6{\cdot}561\ (1)$ Å, $V = 2556\ (1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}524$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}96$ cm^{-1}, $F(000) = 1216$, room temperature, $R = 0{\cdot}060$ for 1795 unique reflections. (3): $M_r = 370{\cdot}41$, monoclinic, $P2_1/c$, $a = 12{\cdot}101\ (6)$, $b = 18{\cdot}658\ (7)$, $c = 7{\cdot}584\ (2)$ Å, $\beta = 90{\cdot}26\ (3)°$, $V = 1712\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}437$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 7{\cdot}92$ cm^{-1}, $F(000) = 776$, room temperature, $R = 0{\cdot}043$ for 1897 unique reflections. In (1) the two carbon atoms of the central double bond [1·339 (3) Å] are pyramidalized, and the double-bond system deviates from planarity by 22·1 (2)°. This is the largest deviation yet reported for this type of distortion. In (2) dichlorocarbene has added to the *exo*-face of (1). The two independent molecules have short intramolecular contacts, Cl···O = 2·567 (6) and 2·568 (6) Å and Cl···H = 2·05 and 2·14 Å. Carbon atoms forming the C(2)—C(3) bond in the phenyl ring are slightly pyramidalized but in a direction opposite to that normally observed in sesquinorbornene-type systems. This is attributed to an attractive interaction between the *endo* hydrogens H(6) and H(7) and the π system of C(2) and C(3). The four C(sp^2)···H distances in the two independent molecules range from 2·18 to 2·27 Å. Compound (3) is formed by the reaction of (1) with anthranilic acid. By a yet not understood mechanism an *N*-formylindazolone moiety is formally added to the reactive double bond. The resulting tricyclic fragment is forced through intramolecular contacts to be planar which leads to extensive electron delocalization. The C(2) and C(3) atoms of the phenyl ring are pyramidalized, and the associated π system deviates from planarity by 3·4 (3)°.


(1)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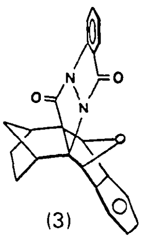
(3)

Introduction. The variation in reactivity of carbon–carbon double bonds due to the electronic effects of substituents and to perturbations by geometric distortions are, in principle, well understood. However, the study of *syn*- and *anti*-sesquinorbornene, (4) and (5), led to the investigation of some unusual stereoelectronic properties of the π systems (Bartlett, Blakeney, Kimura & Watson, 1980). The π system in the *endo* anhydride of the *anti* isomer (5) is essentially planar in the solid state while the nominally sp^2 carbon atoms in two derivatives of the *syn* isomer are pyramidalized, and the π system deviates from planarity by 16–18° (Watson, Galloy, Bartlett & Roof, 1981). A similar hinge-like distortion was observed in *syn*-oxasesquinorbornene anhydride (6) (Hagenbuch,

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† (1*R**, 4*S**, 9*S**, 10*R**) conformation.

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