

**Co-ordination Chemistry of Macrocyclic Polyethers.¹ An Unusual
Conformation of Complexed 18-Crown-6; X-Ray Crystal and
Molecular Structure of a 1:2 Host-Guest Complex of
18-Crown-6 with Benzenesulphonamide**

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Summary In the 1:2 host-guest complex formed between 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6) and benzenesulphonamide, the crown ether adopts nearly the same conformation as the uncomplexed hexaether; the complex is held together mainly by N-H...O hydrogen bonds.

THE ability of crown ethers to form host-guest complexes with alkaline earth metal cations and ammonium salts is well known.² Preliminary X-ray crystallographic results of Dunitz *et al.*³ shows that 18-crown-6 exists in different

conformations in free and complexed forms. X-Ray crystal structure determinations of complexes of crown ethers with CH₃⁴ and OH-acid⁵ substrates show that the crown ether in these compounds adopts a conformation with *D*_{3d}-symmetry which is typical of potassium complexes.

We report the solid-state structure of the product of reaction of 18-crown-6 with the NH-acid substrate, benzenesulphonamide, which can be obtained by a method similar to that used earlier for other compounds.⁶ Crystals of the complex are obtained as colourless needles, m.p. 365 K, which gave satisfactory microanalytical data.

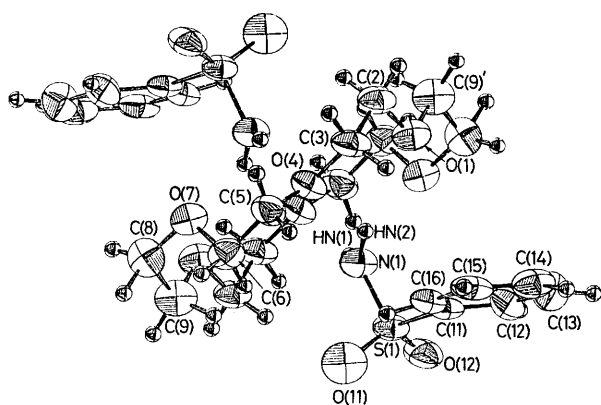


FIGURE. ORTEP drawing of the 1:2 complex of 18-crown-6 with benzenesulphonamide. Bond distances (pm) and angles ($^{\circ}$) are: O(11)–S(1), 143.0(2); S(1)–O(12), 142.2(2); S(1)–N(1), 160.6(2); S(1)–C(11), 178.2(3); C(11)–C(12), 137.6(4); C(11)–C(16), 136.6(4); C(12)–C(13), 137.2(4); C(13)–C(14), 137.9(4); C(14)–C(15), 137.9(4); C(15)–C(16), 139.4(5); O(1)–C(2), 140.8(4); C(2)–C(3), 151.4(5); C(3)–O(4), 141.1(4); O(4)–C(5), 140.6(4); C(5)–C(6), 149.6(3); C(6)–C(7), 142.0(3); O(7)–C(8), 144.7(3); C(8)–C(9), 148.9(4); C(9)–O(1'), 142.1(4); N(1) \cdots O(7), 303.8(4); N(1) \cdots O(1), 310.0(4); N(1) \cdots O(4), 299.6(4); HN(2) \cdots O(4), 199.4; HN(1) \cdots O(4'), 233.7; \angle O(11)–S(1)–O(12), 119.8(1); \angle O(11)–S(1)–N(1), 107.0(1); \angle O(12)–S(1)–N(1), 107.7(1); \angle O(11)–S(1)–C(11), 105.7(1); \angle O(12)–S(1)–C(11), 108.0(2); \angle N(1)–S(1)–C(11), 108.1(2); \angle S(1)–C(11)–C(12), 119.6(2); \angle S(1)–C(11)–C(16), 120.0(2); \angle C(12)–C(11)–C(16), 120.3(3); \angle C(11)–C(12)–C(13), 119.7(2); \angle C(12)–C(13)–C(14), 121.1(2); \angle C(13)–C(14)–C(15), 118.9(3); \angle C(14)–C(15)–C(16), 120.0(2); \angle C(11)–C(16)–C(15), 119.9(2); \angle C(9')–O(1)–C(2), 111.4(2); \angle O(1)–C(2)–C(3), 109.3(3); \angle C(2)–C(3)–O(4), 109.7(3); \angle O(4)–C(5)–C(6), 110.2(2); \angle C(3)–O(4)–C(5), 113.8(2); \angle C(5)–C(6)–O(7), 109.2(2); \angle C(6)–O(7)–C(8), 112.5(2); \angle O(7)–C(8)–C(9), 113.3(3); \angle C(8)–C(9)–O(1'), 109.7(2); \angle N(1) \cdots O(4) \cdots HN(2), 3.3; \angle O(4) \cdots HN(2) \cdots N(1), 170.1; \angle HN(2) \cdots N(1) \cdots O(4), 6.6. Torsion angles are: C(9')–O(1)–C(2)–C(3), 176.7; O(1)–C(2)–C(3)–O(4), -65.8 ; C(2)–C(3)–O(4)–C(5), 157.6; C(3)–O(4)–C(5)–C(6), 180.0; O(4)–C(5)–C(6)–O(7), -66.6 ; C(5)–C(6)–O(7)–C(8), 180.0; C(6)–O(7)–C(8)–C(9), -72.5 ; O(7)–C(8)–C(9)–O(1'), -68.4 ; C(8)–C(9)–O(1')–C(2'), 172.9.

All torsion angles about the C–C bonds of the crown ether in the complex are nearly 65° . In this respect the structure of the polyether differs from that of the uncomplexed molecule.³ The Figure shows an ORTEP drawing of the complex viewed in direction of the mean plane of the polyether.

Crystal data: $C_{24}H_{38}N_2O_{10}S_2$, M 578.7, monoclinic, space group $P2_1/a$, $a = 1004.0(1)$, $b = 1465.9(2)$, $c = 965.5(1)$ pm, $\beta = 94.2(1)^{\circ}$, $U = 1.4172 \times 10^9$ pm³, $Z = 2$, $D_c = 1.36$ g cm⁻³, $F(000) = 612$, $R = 0.059$ at the present stage of refinement for 1935 independent reflections collected on a Syntex $P2_1$ diffractometer (Cu- $K\alpha$). The structure was solved by direct methods.⁷ The positions of the hydrogen atoms were refined.[†]

The crown ether molecule in the complex lies about a crystallographic centre of symmetry which relates the two guest benzenesulphonamide molecules which are hydrogen-bonded to the crown ether. The N \cdots O distances are not equal [N(1)–O(1), 310.0; N(1)–O(4), 299.6; N(1)–O(7), 303.8 pm]. Therefore, different N–H \cdots O interactions can be observed including a strong one with an H \cdots O distance of 199.4 pm [HN(2) \cdots O(4)] and an O(4)–HN(2)–N(1) angle of 170.1° and probably a weak one with an H \cdots O distance of 233.7 pm [HN(1) \cdots O(4')]. The formation of a strong hydrogen bond as well as a weak one is, therefore, not due to the D_{3d} -symmetry of the crown ether. The observed elliptical shape, compared with the nearly-circular conformation in most similar complexes, shows the ability of 18-crown-6 to change its conformation not only in charged but also in uncharged host-guest complexes to fit the guest molecule in the best possible way.

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[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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