

Crystal and Molecular Structure of Benzo-27-crown-9 Guanidinium Perchlorate (1 : 1): an Encapsulated Complex

Jos W. H. M. Uiterwijk,^{a*} Sybolt Harkema,^a Jan Geevers,^b and David N. Reinhoudt^b

^a Chemical Physics Laboratory and ^b Laboratory of Organic Chemistry, Twente University of Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands

In the crystal structure of the complex of benzo-27-crown-9 and guanidinium perchlorate (1 : 1) a complementary binding relationship between host and guest is found; all guanidinium hydrogen atoms are involved in hydrogen bonding to oxygen atoms of the macrocycle.

At present there is considerable interest in the synthesis of macrocyclic receptors, which can bind small organic molecules like guanidinium ions and urea molecules selectively. Such a selective binding requires a complementary relationship between the bonding possibilities of host and guest.

Complex formation between a crown ether and guanidinium ions was first mentioned by Pedersen,¹ who reported complexes of dibenzo-18-crown-6. From the crystal structures of complexes of 18-crown-6 with guanidinium nitrate² and urea³ it is clear that not all possible hydrogen bonding interactions between host and guest are used, the cavity of the host being too small to accommodate the guest.

Guanidinium complexes with larger macrocycles were reported for benzo-27-crown-9^{4,5} and for a 27-crown-9 hexacarboxylate.⁶ From the fact that guanidinium ions can be used as templates in the synthesis of benzo-27-crown-9, Cram *et al.*^{4,5} have postulated that the guanidinium ion fits very well in the cavity of the benzo-27-crown-9 molecule, but this assumption has not been verified so far by means of an *X*-ray structure determination.

A molecular complex of benzo-27-crown-9 and guanidinium perchlorate was obtained by equilibration of a solution of benzo-27-crown-9 (1 mmol) in chloroform (2 ml) with a solution of guanidinium sulphate (1 mmol) and lithium perchlorate (1 mmol) in water (2 ml). The chloroform layer was dried (MgSO₄) and evaporated, and the crystalline product was purified by trituration with ether and subsequent recrystallisation from ethanol: m.p. 111–113 °C.†

The crystal structure of the complex at 156 K was determined by *X*-ray crystallography.

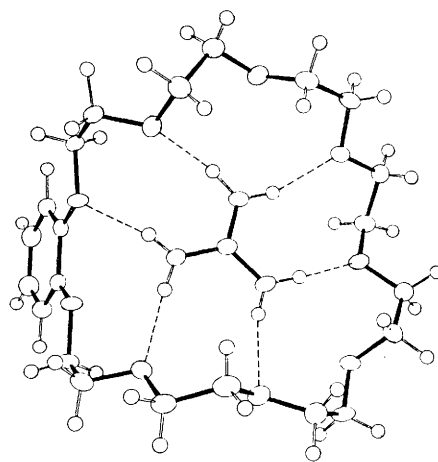


Figure 1. ORTEP⁸ view from above of one of the benzo-27-crown-9 molecules with the guanidinium cation belonging to it. The hydrogen bonds are indicated by broken lines.

Crystal data: C₂₃H₄₂ClN₃O₁₃, orthorhombic, space group *Pbca*, *a* = 28.397(5), *b* = 8.633(2), *c* = 23.495(5) Å, *Z* = 8, *D*_c = 1.397 g cm⁻³. 5121 reflexions were measured using the ω -2 θ scan mode (2 < θ < 74.5°) on a Philips PW1100 diffractometer with graphite-monochromated Cu-K α radiation.

4373 reflections with *I* > $\sigma(I)$ (from counting statistics) were used for the solution by direct methods.⁷ All hydrogen atoms were located in a difference Fourier map. The structure was refined by least-squares methods to a final weighted *R*-

† Satisfactory elemental analyses were obtained.

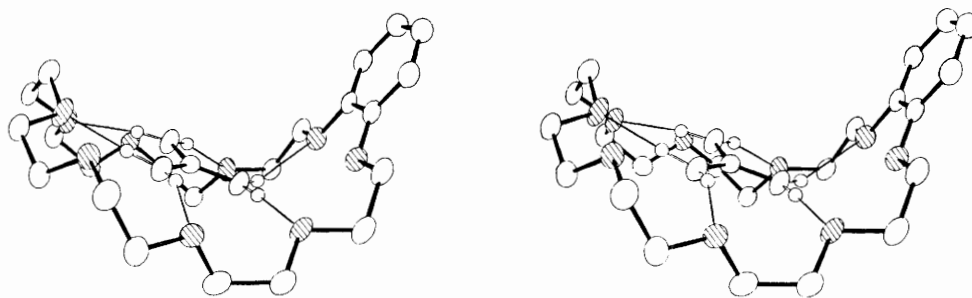


Figure 2. Stereoscopic ORTEP⁸ view from the side of the benzo-27-crown-9.C(NH₂)₃⁺ complex. The crown hydrogens are omitted for clarity. Oxygen atoms are shaded.

factor of 7.7% (anisotropic thermal parameters for non-hydrogen atoms, isotropic for hydrogen atoms).[‡]

The benzo-27-crown-9 ring has a fairly irregular conformation. The sequence of the torsion angles (C–O–C–C, O–C–C–O, C–C–O–C *etc.*) is: asa ag⁻a ag⁻a ag⁺g⁺ ag⁺a g⁻g⁻a ag⁻a g⁻g⁻ ag⁺a.[§]

The guanidinium ion is nested within the macrocyclic receptor (Figure 1). Each nitrogen atom is bonded *via* both hydrogen atoms to next-neighbour crown oxygen atoms. The N...O distances vary between 2.84 and 3.08 Å, whereas the N–H...O bond angles range from 148 to 177°.

Besides the H-bonding stabilisation of the complex, there seems to be an electrostatic contribution from the three non-hydrogen-bonded crown ether oxygen atoms with the nitrogen atoms (N...O distances: 2.99–3.14 Å).

The ring not only has the wreath-shaped structure suggested by several authors,^{4–6,9,10} but moreover forms a sort of bowl, the guanidinium ion 'lying' on the bottom (Figure 2).

[‡] 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.

[§] 's' (synperiplanar) denotes an O–C–C–O torsion angle of almost 0°, imposed by the benzo-substituent. The sequence of torsional angles in the text reads anticlockwise in Figure 1 starting with the benzo-group. Complete details of the structure will be published elsewhere.

The structure of the guanidinium benzo-27-crown-9 complex represents an example of an organic molecule completely encapsulated within the cavity of a macrocyclic polyether. From the complementary host–guest relationship found the template function of guanidinium ions in the synthesis of benzo-27-crown-9 can be understood.

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