The *X*-Ray Crystal Structure of an Ethyl Cinnamate–β-Cyclodextrin Guest–Host Complex

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An *X*-ray crystallographic determination of the structure of the title complex reveals that the ester function protrudes from the torus at the side bearing primary hydroxy-groups; this strengthens recent rationalisations of the electro-organic reactions of such complexes.

Cyclodextrins, through guest–host complexation, accelerate several organic reactions and, in particular, such systems have been used as models for hydrolytic enzymes.[1] Recently it has been shown that complexation with β-cyclodextrin can substantially modify the course of cathodic reactions[2] and also that β-cyclodextrin, substituted at the 6-position with an electrophore, is a model for a redox enzyme.[3] Guest–host complexes are key intermediates in these reactions and, using 400 MHz ^{1}H n.m.r. spectroscopy,[2] the shielding effects of aromatic ring currents on protons inside the torus may be used to establish that in solution the complexes include the aromatic portion of such molecules as acetophenone, benzyl esters, aromatic aldehydes, and ethyl cinnamate. A detailed description of the mechanism for redox catalysis[3] and for the observed changes in the course of electro-organic reactions also requires knowledge about the environment of the polar reaction centre. In the rationalisation of results concerning ester hydrolysis it has been commonly assumed that the polar groups protrude from the side of the torus bearing the more acidic, secondary hydroxy-groups.

We report herein the first *X*-ray crystallographic structure determination of a cyclodextrin complex of which the electrochemical reactions have been studied in detail. The complex crystallises in the stable, triclinic CI form[4] in which pairs of cyclodextrin molecules form a cage to accommodate the guests (as distinct from the CII form in which the guests occupy channels).

Crystal data: $[(C_{42}H_{70}O_{35})_2(C_{11}H_{10}O_2)\cdot 17.5H_2O]$, M = 2761.5, triclinic, a = 18.186(3), b = 15.486(2), c = 15.392(2) Å, α = 102.78(1), β = 113.61(1), γ = 99.74(1)°, U = 3725 Å^3, space group $P\bar{1}$, Z = 1, D_c = 1.23 g cm^{-3}, λ (Cu-K_α) = 1.54178 Å.

The structure was determined by the isomorphous replacement method, using the co-ordinates of the cyclodextrin molecules found for the n-propanol complex[5] and refined by

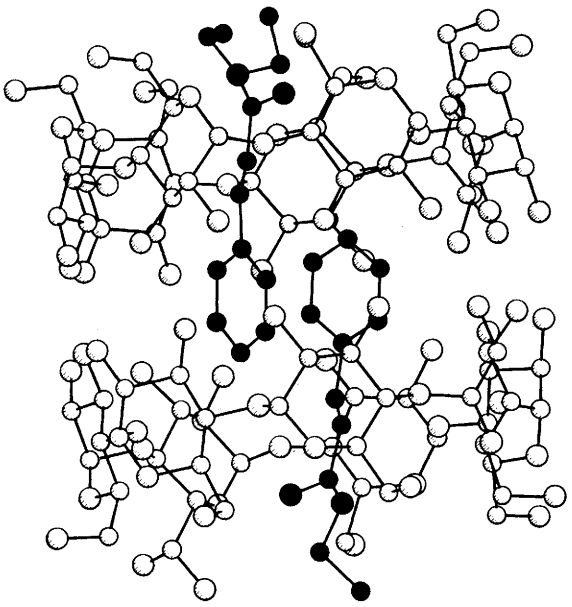
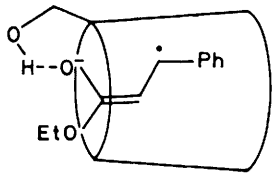


Figure 1

least squares, using intensity data {11057 recorded, 7984 observed $[I>1.5\sigma(I)]$} measured on a CAD4 diffractometer, to a current R value of 0.123.† Figure 1 gives a side view of the cage-forming cyclodextrin dimer (view direction [010]): the guest molecule, shown fully shaded, half occupies two distinct sites. In one of these sites the ethyl unit is disordered over two positions. The figure shows that, in the solid state, the polar reaction centre (–CH:CHCO$_2$Et) protrudes from the side of the primary hydroxy-groups.

† 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 requests should be accompanied by the full literature citation for this communication.



(1)

Cathodic reduction of the ethyl cinnamate complex in *N,N*-dimethylformamide solution gives predominantly hydrogenation of the double bond rather than hydrodimerisation which predominates in the absence of strong proton donors.[2] Although for dynamic equilibrium in solution it is possible that both orientations of the host are present, the clear establishment of the above structure lends great support to the key protonation of the cinnamate radical-anion involving a transition state such as (**1**). A rationalisation of the redox reactions previously reported also requires that the polar reaction centre can protrude at the side of the primary hydroxy-groups. It is on that side that the electrophore is attached and its observed interaction, in the reduced form, with the guest molecules (benzyl esters) is now readily explained.

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References

1 M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,' Springer–Verlag, New York, 1978.
2 C. Z. Smith and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, 1981, 492.
3 C. Z. Smith and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, 1981, 792.
4 J. J. Stezowski and K. Jogun, *Nature*, 1978, **278**, 667.
5 J. J. Stezowski and K. Jogun, personal communication.