Transient Binding Mode of Phenolphthalein–β-Cyclodextrin Complex: The Lactone Dianion as an Induced Transition-state Analogue Trapped in β-Cyclodextrin

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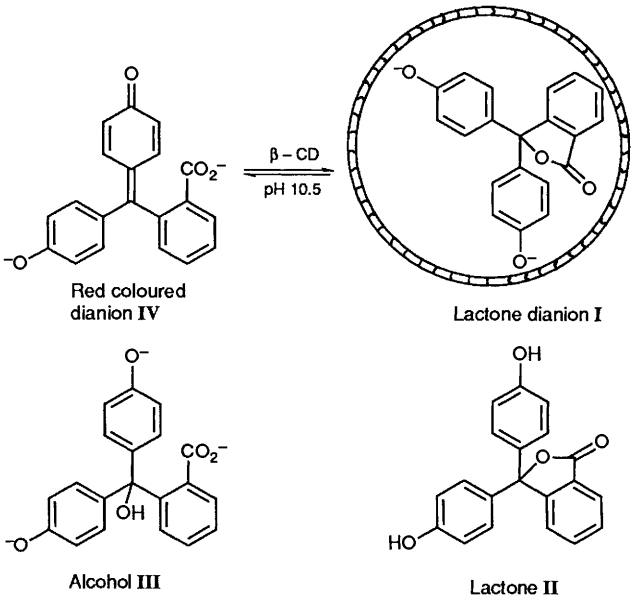
^{1}H and ^{13}C NMR spectroscopy of phenolphthalein disodium salt–β-cyclodextrin complex in Me_2SO, and in mixtures of Me_2SO–D_2O, further supports the lactone dianion structure in the complex as a new and hitherto unforeseen form of phenolphthalein; the aryl residue bearing the lactone ring has penetrated the cavity, whereas both phenolate anions are held on the rim to modulate sensitively the binding mode of the complex, and the optimal space-filling molecular model shows that the lactone dianion has a remarkable close fitting contact to a β-CD, and also indicates that the distortion caused by the two phenolic groups on the shape of β-CD is a prerequisite and essential part of the subsequent structural transformation, destroying the quinone–phenolate system of the red-coloured phenolphthalein dianion to become flat on the rim, that is to adopt a conformation complementary to that of β-CD; in this way, the lactone-dianion is formed as an induced transition-state analogue trapped in β-CD for the enantiomerization of the helical three aromatic rings of a red coloured phenolphthalein in solution.

As part of our previous report on the phenolphthalein–β-cyclodextrin complex (PP–β-CD complex) as a simple chemical model for enzymic systems,[1] the colourless transient binding mode of PP within the field of a β-CD molecule was presented as the lactone dianion structure **I** on the basis of the ^{13}C NMR spectroscopy (Scheme 1). However, it was pointed out[2] that the ^{13}C NMR spectrum of the red coloured dianion **IV** alone in dimethyl sulfoxide (DMSO) shows a similar pattern[3] to that of PP–β-CD complex in aq. solution at pD 10.5,[1] and a new form of dianion that has a positively charged sp^3-central carbon atom (C-1) was proposed instead; this carbenium ion was hydrogen-bonded through a water bridge to the carboxylate anion without forming a lactone ring, and one of the phenolic groups had penetrated the cavity. The tight binding nature of this complex was attributed to the hydrogen-bonding of the two phenolic oxygen atoms each to a hydroxy group of the β-CD molecule.

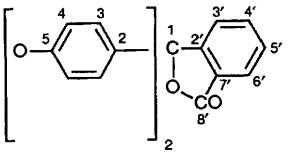
First and foremost, however, since the two phenolic groups of PP are indeed ionized in the complex,[1,2] one naturally knows that the quinone structure is lost. Then, the next question to be answered is 'what substituent occupies the fourth valence site of the central carbon atom (C-1)'; it is not a hydroxy group like that in the tertiary alcohol **III**. When one compares the chemical shifts for the key carbon atoms of the lactone portion of the transient binding mode of PP (**I**) at C-1 δ_C 95.59; C-2′ 154.07; C-7′ 125.12; and C-8′ 173.85 with those for the tertiary alcohol **III** bearing the carboxylate anion without forming a lactone ring at C-1: δ_C 82.57; C-2′ 146.75; C-7′ 139.97; and C-8′ 179.08,[1] these chemical shifts of the corresponding carbon atoms is readily recognized to be significantly different by amounts ranging from 5 to 15 ppm. Further, this fourth substituent is not one of the hydroxy groups of a β-CD molecule, because the chemical shifts for the carbon atoms of β-CD were observed almost unchanged (±0.2 ppm) from those of the corresponding carbon atoms of a free β-CD, and no sign of splitting of these resonances was noted. The remaining functionality is the carboxy group of PP. It is this carboxy group that can form the lactone ring with the central carbon atom (C-1). The chemical shifts for the carbon atoms of the transient binding mode of PP (**I**) are indeed in accord with those for the corresponding carbon atoms of the un-ionized lactone form **II**.[1] Some differences observed in the chemical shifts can be ascribed to the ionization of the phenolic protons. Thus, one can reasonably deduce that the transient binding mode of PP is that of the lactone dianion structure **I**.



Scheme 1 The structural forms of phenolphthalein

In this paper, we shall first present the results of ^{1}H and ^{13}C NMR spectroscopic analyses of PP–β-CD complex in Me_2SO, and also in mixtures of Me_2SO–D_2O, to compare them with the previous measurements in D_2O at pD 10.5, measurements further supporting the lactone dianion structure **I** where the aryl residue bearing the lactone ring has penetrated the cavity, while the two phenolate anions are held on the rim of a β-CD moiety. The reaction mechanism of this lactonization, as well as the tight binding nature of the complex, will then be discussed from the viewpoint of optimal space-filling molecular models.

Table 1 ^{13}C Chemical-shift changes of phenolphthalein



Assignment[a]	δ_C for lactone dianion **I** in $(CD_3)_2SO$	δ_C for lactone dianion **I** in D_2O, pD 10.5[b]	δ_C for lactone **II** in $(CD_3)_2SO$[b]
C-1	94.33	95.59	92.83
C-2	123.75 123.86	129.19 130.08	132.61
C-3	127.63 127.80	128.71 129.33	129.56
C-4	117.37	117.9 118.6	116.63
C-5	166.64 166.73	162.90 163.78	158.92
C-2′	153.75	154.07	153.97
C-7′	124.58	125.12	125.90
C-3′	124.16	124.61	125.80
C-4′	133.87	136.67	136.09
C-5′	128.28	130.86	130.87
C-6′	124.37	126.78	126.70
C-8′	169.55	173.85	170.48

[a] Chemical shifts for the aryl carbon atoms of C-3′ to C-6′ were previously assigned as a group.[1] Each chemical shift herein was assigned on the basis of the 2-D INADEQUATE spectrum of the lactone **II**[5] that showed agreement with the assignments of ref. 3. DEPT Spectra were also utilized for the assignments of the shifts for the carbon atoms of the PP–β-CD complex in Me_2SO solution. [b] Chemical shifts cited from ref. 1.

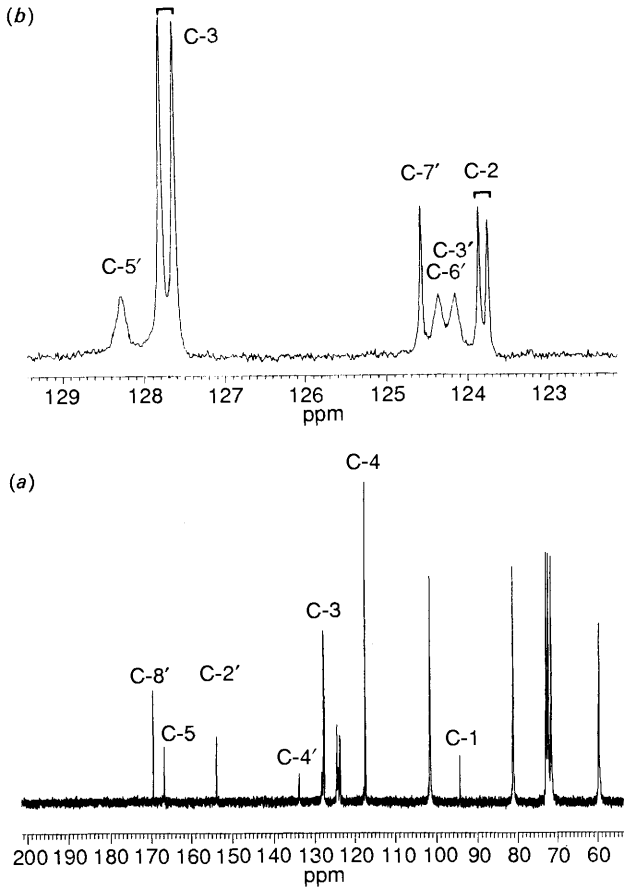


Fig. 1 (*a*) ^{13}C NMR spectrum of the transient binding mode of lactone dianion **I** in Me_2SO at a probe temperature of 300 K. The molar concentration was 0.1 mol dm^{-3} for each component (disodium salt of PP and β-CD). (*b*) Part of spectrum (*a*) is enlarged.

Results and Discussion

^1H *and* ^{13}C *NMR Studies.*—The red colour of the PP dianion **IV** in the dipolar, aprotic solvent Me_2SO was found to disappear instantly when β-CD was added to the solution, just as it does in aq. solution. The ^1H and ^{13}C NMR spectra of the complex were recorded with the samples prepared with phenolphthalein disodium salt and β-CD dissolved in appropriate solvents, and the representative results are gathered in Table 1 and Figs. 1 and 2.

In Me_2SO solution, the ^{13}C NMR chemical shift for the central carbon atom (C-1) of the colourless, bound form of PP in the complex appeared at δ_C 94.33. This is in accord with the previously recorded value of δ_C 95.59 in aq. solution at pD 10.5, but distinctly different from the value for the red coloured PP dianion **IV** alone in Me_2SO as solvent (δ_C 100.07).[3] This evidence, together with the chemical shifts for the remaining key carbon atoms of the lactone portion (C-2′, C-7′ and C-8′) which correspond with each of those for the un-ionized lactone form **II** without substantial differences in the two distinct solvents (Table 1), supports the view that the transient binding mode of the PP–β-CD complex in Me_2SO also has a lactone ring, as in aq. solution at pD 10.5. Since the two phenolic groups are completely ionized in Me_2SO, the structure is that of the lactone dianion **I**.

The solvent effect was, however, noticed for the ^{13}C chemical shifts of the aryl residue bearing the lactone ring (C-3′, C-4′, C-5′ and C-6′): $\Delta\delta_C$ 1–3 ppm. A large difference for the C-2 carbon atom of the phenolate anion was observed in Me_2SO (δ_C 123.75 and 123.86) from the previously recorded value in D_2O at pD 10.5 (δ_C 129.19 and 130.08). This resonance appeared clearly as a pair of split resonances caused by the enantiotopic environments of the two sets of C-2 carbon atoms of the phenolate anions. Similarly, significant differences in the chemical shifts of the red coloured, ionized PP **IV** in Me_2SO were reported[3] from those in aq. solution.[1] These differences can be most reasonably ascribed to the strong dipolar, aprotic and polarizable nature of Me_2SO in contrast to protic D_2O. However, this solvent effect was found to have less influence on all the ^{13}C chemical shifts of the un-ionized lactone form **II**, which were observed practically unchanged regardless of the solvent used: Me_2SO,[1,3] Polyol,[4] and a mixture of Me_2SO and D_2O (9:1, v/v).[5] Therefore, it should be noted that, although the relatively solvent-insensitive chemical shifts for the lactone-ring portion (C-1, C-2′, C-7′ and C-8′) provide a satisfactory basis for the direct comparison of the chemical shifts for the various forms of PP in different solvents, the ^{13}C NMR chemical shifts for the carbon atoms of the red coloured dianion **IV** in Me_2SO, as well as those for the several carbon atoms of the ionized aromatic residues of PP in Me_2SO, are susceptible to Me_2SO as solvent relative to D_2O; thus, they should not be used for direct comparison of the ^{13}C chemical shifts for the various ionic forms of PP in different solvents as, for example, in the discussion basis of ref. 2.

In Fig. 2 the ^1H NMR spectra of PP in the complex are presented to supplement the ^{13}C NMR spectral data. The resonances of the hydrogen atoms of the aryl residue bearing the lactone ring (3-H′, 4-H′, 5-H′ and 6′-H), and those of the two phenolate anions (3-H and 4-H) are indeed affected by the change in Me_2SO–D_2O composition. This feature in turn supports the claim that the differences observed in the chemical shifts of the corresponding carbon atoms are due to the solvent

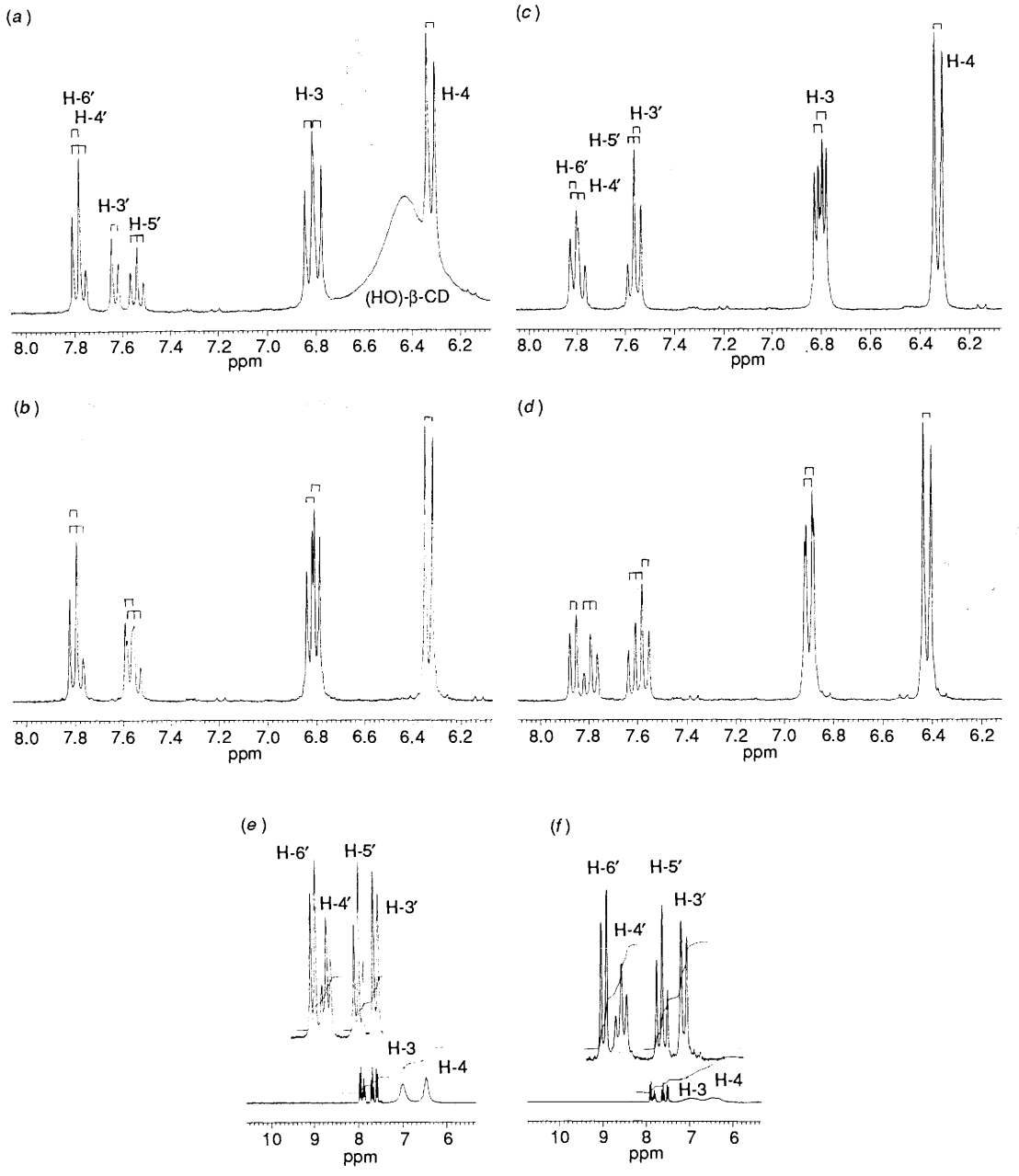
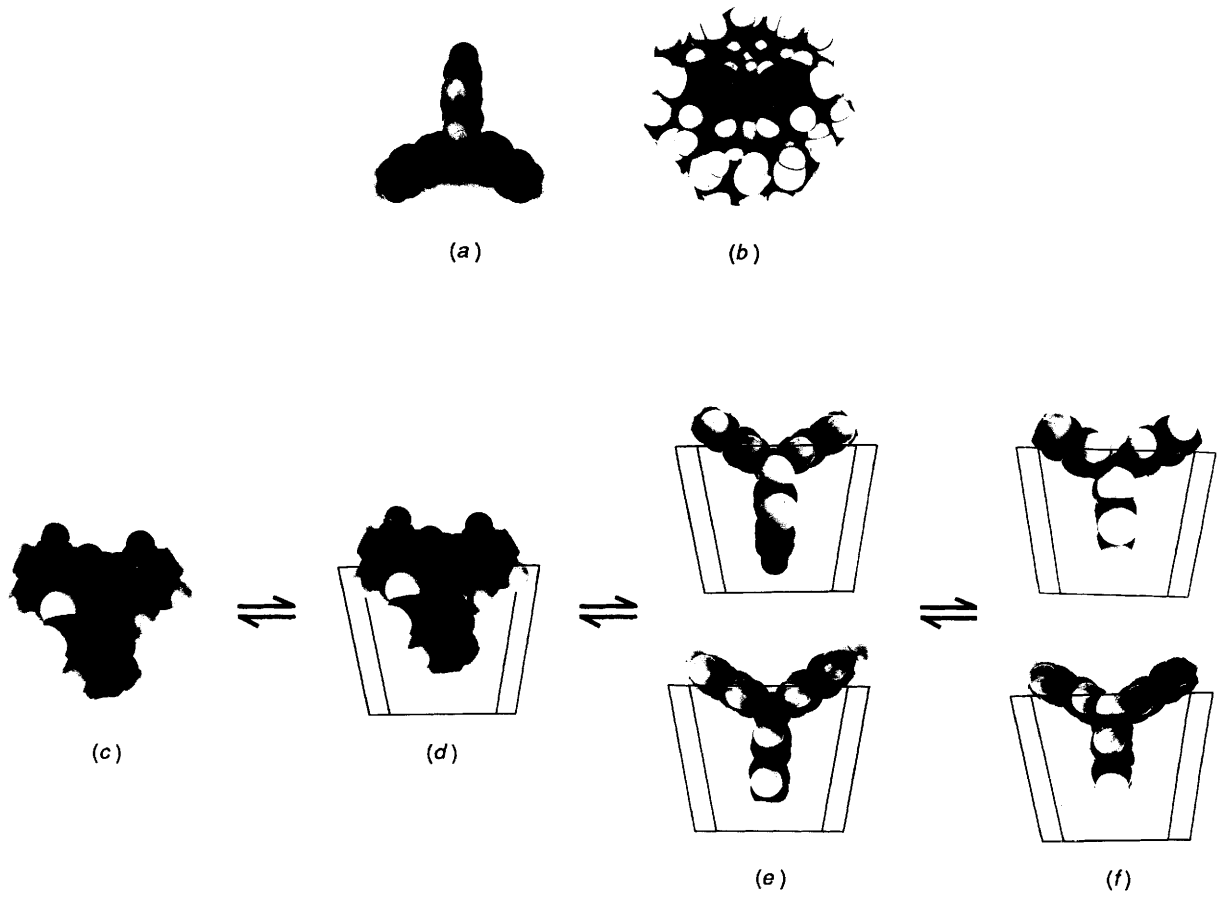


Fig. 2 ^{1}H NMR spectrum of the transient binding mode of lactone dianion **I** at a probe temperature of 300 K. The molar concentration was 0.02 mol dm^{-3} for each component (disodium salt of PP and β-CD): (*a*) in Me_2SO, (*b*) in Me_2SO with a few drops of D_2O, (*c*) in Me_2SO–D_2O (9:1, v/v), (*d*) in Me_2SO–D_2O (1:1, v/v) (*e*) in Me_2SO–D_2O (1:4, v/v), (*f*) in D_2O.

effect, perhaps coupled with solvent perturbation to the binding mode of the PP–β-CD complex. The resonance of the 3′-H hydrogen atom sensitively moved upfield, away from those of 4′-H and 6′-H, as the D_2O content of the solvent was increased, and even crossed over the resonance of the 5′-H hydrogen atom (see Fig. 2). Although each resonance of the 3-H hydrogen atoms of the phenolate anions was split into a pair of resonances due to the enantiotopic environments in the complex in Me_2SO, the width of this separation became narrower with increasing content of D_2O in the solution. Furthermore, in D_2O, the ^{1}H resonances of both the 3-H and 4-H hydrogen atoms were observed to broaden, and they both coalesced (Fig. 2*e* and 2*f*), and the corresponding ^{13}C resonances for the carbon atoms of the phenolate anions were also observed to coalesce in D_2O, although the ^{13}C NMR spectra are not displayed in this paper.

The above features are an important indication that the motional restriction on the alignments of the two phenolate anions with respect to a β-CD moiety became relaxed upon addition of D_2O; the 3-H hydrogen atoms of the phenolate anions, and the 4-H hydrogen atoms as well, begin to move and feel the average field of their different environments. Since an apparent pD-value of 11.4 was noted for the sample solution, some of the secondary hydroxy groups of the β-CD (pK_a ~12.1)[6] are expected to be ionized to repel the nearby phenolate anions. This simultaneous onset of the movements of the two phenolate anions upon addition of D_2O can be physically possible when both phenolate anions are positioned on the rim of a β-CD, while the aryl residue bearing the lactone ring penetrates the cavity, because all the resonances of the hydrogen atoms of both phenolate anions in the complex simultaneously coalesced to the same extent and in the same way (Fig. 2*e* and 2*f*) as the D_2O content was increased. Alternatively, if the binding mode were to have one of the



Scheme 2 The space-filling molecular models for the reaction mechanism of the lactonization catalysed by β-CD. Carbon atoms, black; hydrogen atoms, grey; oxygen atoms, larger grey. (*a*) Lactone dianion **I**; (*b*) PP–β-CD complex; (*c*) red coloured dianion **IV**; (*d*) red coloured dianion **IV** in a β-CD cavity; (*e*) the distorted structure of the quinone–phenolate system in a β-CD cavity; (*f*) lactone dianion **I** in a β-CD cavity.

phenolate anions penetrating the cavity with the other being held on the rim, the motional behaviour of the two phenolate anions would naturally be expected to be quite different, so the resonance broadening of the 3-H and 4-H hydrogen atoms should have revealed this difference. Furthermore, the rapid exchange of their mutual positions between that in the cavity and that on the rim to average out the geometrical difference of the two phenolate anions is physically unlikely, and this possibility can be excluded from consideration.

Despite the increased motion of the phenolate anions on the rim of a β-CD molecule, the corresponding ^{13}C chemical shifts for the key carbon atoms of the lactone portion remained almost unchanged in D_2O: C-1 δ_C 95.55; C-2′ 153.37; C-7′ 125.22; C-8′ 172.95 when compared with the corresponding values in Me_2SO, and also with those in aq. solution at pD 10.5 (Table 1), indicating that the lactone ring is still bound in the cavity of the β-CD under these perturbed conditions.

Based on the previous [1] and the present results, the transient binding mode of PP–β-CD complex, although not a stationary structure, can be reasonably deduced to be that of the lactone dianion **I** that has the aryl residue bearing the lactone ring penetrating into the cavity, and the two phenolate anions being held on the rim to modulate sensitively the binding mode of the complex in solution.

Reaction Mechanism of the Lactonization.—The optimal space-filling molecular model also supports the above structure of the PP–β-CD complex. As discussed previously, this lactonization reaction proceeds through the transformation of the red coloured, trigonal, sp^2-valence state of the central carbon atom (C-1) to the colourless, tetrahedral, sp^3-valence state to form the lactone dianion **I** under the constraint of a close-fitting binding mode with β-CD.

The red coloured phenolphthalein dianion **IV** has an extended π-electron conjugated system, so the conformation of the three aromatic rings tends to be coplanar. However, owing to the mutual steric hindrance among the three aromatic rings, the predominant ground-state conformation assumes a partially distorted helical form similar to other triarylmethyl derivatives;[7] this system is chiral, but only one of the enantiomers is shown in Scheme 2, structure (*c*). The following reaction mechanism of the lactonization can therefore be envisaged. When the aryl residue bearing the carboxylate anion of the red-coloured dianion **IV** penetrates the cavity of a β-CD to form an initial encounter complex, the two phenolic groups constituting the quinone–phenolate system stand perpendicular to the plane of the rim of the β-CD moiety [Scheme 2, (*d*)]. This conformation requires further distortion to fit more perfectly to the β-CD; *i.e.*, the two phenolic groups must be brought to rest flat on the rim. This can be achieved by rotating the three helically arranged aromatic rings around each bond of the central carbon atom (C-1) at the expense of destroying the energetically favourable quinone–phenolate system of the extended π-electron conjugation. This step results in the reactive conformation where all three planes of the aromatic rings are positioned perpendicular to the plane of the trigonal sp^2-valence state of the carbenium ion-like central carbon atom (C-1), as can be seen in Scheme 2, (*e*). This is the most significant high-energy state of the phenolphthalein dianion **IV** in the absence of β-CD, but this conformation can virtually be generated by the strong binding energy provided by β-CD. It

should be noted that the space-filling molecular model shows that this conformation [Scheme 2, (*e*)] remarkably resembles the lactone dianion structure **I** as shown in Scheme 2, (*f*).

Since the oxygen atom of the carboxylate anion now comes into a position quite close in front of the carbenium ion-like trigonal sp^2-central carbon atom (C-1), this carboxylate anion can readily form the lactone ring; that is, once the initial encounter complex is formed, the lactonization reaction can proceed spontaneously without any further requirement of free energy of activation, and without any further entropy loss, to stabilize the positively charged, energetically unfavourable central carbon atom (C-1) by transforming the trigonal sp^2-valence state into the tetrahedral sp^3-valence state. During this stage, the aromatic residue bearing the lactone ring moves backward to be embraced more closely by the β-CD [Scheme 2, (*e*) and (*f*)]. In this way, the lactone dianion **I** becomes an induced transition-state analogue trapped in a β-CD for the enantiomerization reaction of a red coloured phenolphthalein dianion **IV** in solution.

Space-filling molecular models also revealed that the rotational motion of the aryl residue bearing the lactone ring is strongly restricted in the cavity of a β-CD molecule, as also are restricted the rotational motions of the two phenolate anions, since they are held on the rim. Therefore, all the internal rotational freedoms of the lactone dianion **I** are almost lost in the β-CD. This aspect is in accord with previous measurements of the ^{13}C NMR spin-lattice relaxation times (T_1);[1] the most tightly bound site is the aryl residue bearing the lactone ring, and the two phenolate anions are bound relatively less tightly on the β-CD, but they are restricted enough in motion.

When bulky substituents are attached to the phenolic groups, such as in *o*-cresolphthalein or thymolphthalein, then the quinone–phenolate system of the two phenolic groups is apparently lifted from the rim of the β-CD, and the carboxylate anion or the lactone-ring portion tends also to be lifted to decrease the penetration-depth into the cavity. When the two phenolic groups are linked with an oxygen atom as in fluorescein, the quinone–phenolate system of the two phenolic groups cannot be distorted to become flat on the rim, so the substituted phenolphthalein having either the bulky substituents or the oxygen bridge between the two phenolic groups has difficulty in effectively overcoming the energy barrier for structural distortion of the two phenolic groups on the rim, which is a prerequisite and essential part of the subsequent formation of the lactone dianion **I** within the β-CD cavity. Thus, the two phenolic groups on the rim sensitively modulate the binding mode of the PP–β-CD complex.

Although a α-CD can also accommodate the lactone dianion **I**, the cavity size is less wide than that of β-CD. Therefore, the lactone-ring portion cannot penetrate the cavity deeply enough. It is, perhaps, also a crucial factor in this case that the initial encounter complex of PP with an α-CD, *i.e.*, the quinone–phenolate system of the red coloured dianion **IV** standing perpendicularly to the plane of the rim, is markedly less interactive with the α-CD, and less capable of initiating the subsequent distortion of the quinone–phenolate system than was the case with the β-CD system, so formation of the PP–α-CD complex becomes slower, and the complex is looser than for the PP–β-CD complex. This aspect of the slow complex formation is in accord with experimental results,[8] showing that the binding rate with an α-CD is slower by two orders of magnitude compared with that of complex formation with β-CD.

In the alternative binding mode, one of the phenolic groups can smoothly penetrate the cavity of a β-CD; even a substituted phenolic group having either a methyl (*o*-cresolphthalein) or (both groups) a methyl and an isopropyl substituent (thymolphthalein), can readily penetrate the cavity of a β-CD. From the viewpoint of optimal space-filling molecular models, these complexes seem to be readily formed. The alternative binding mode cannot explain the marked differences observed in the formation of the complex of the above substituted phenolphthalein derivatives with a β-CD molecule.

All the above aspects can be completely explained by the present reaction mechanism wherein the aryl residue bearing the carboxylate anion, not the phenolic group, is drawn into the cavity of the β-CD, and this is followed by the critical and essential step of the structural distortion, the destruction of the quinone–phenolate system on the rim, as also evidenced for the PP–β-CD complex by the present NMR studies. Once the initial encounter complex of PP with a β-CD is formed in this way, the maximum close-fitting binding mode determines the rest of the course of the lactonization reaction.

Driving Forces for the Lactonization Reaction.—Several forces are conceivable as being responsible for this lactonization reaction inside a β-CD. Desolvation naturally acts as an important first step. Although the present space-filling molecular model cannot reveal this aspect, the role of structured water for the activation stage for both the association and the dissociation were indicated by previous studies.[1] One of the factors causing difficulty in the penetration of the phenolic oxygen atom into the cavity of a β-CD would be the relative difficulty of desolvation of the solvent molecules surrounding the oxygen atoms of the phenolic groups of the red coloured dianion **IV**. Hydrophobic bonding would ordinarily exist in a situation such as this. Although the red coloured dianion **IV** is not typically apolar as a whole, since each of the three aromatic residues has a potential anionic site, the aryl residue portion bearing the carboxy anion is locally apolar and tends to penetrate the cavity of a β-CD, and becomes entirely apolar when the lactone ring is formed in the cavity. Hydrogen-bonding between the two phenolate anions and the hydroxy groups of a β-CD can also be operative, since space-filling molecular models shows that each oxygen atom of the two phenolate anions and the secondary hydroxy group of β-CD are quite close to each other, and these two sites may act as a pivot for the subsequent structural distortion as shown in Scheme 2. The van der Waals attractive force naturally exists between the penetrated aryl residue bearing the lactone ring and the interior of a β-CD. However, electrostatic forces act in a final and decisive role, since the final step of the lactone-ring formation between the carboxylate anion and the carbenium ion-like central carbon atom (C-1) can be regarded as an electrostatic reaction within the solvent-free, buried part of the β-CD in order greatly to stabilize the positively charged, energetically unfavourable central carbon atom (C-1); that is, this final step for stabilization is coupled with the energy-requiring destruction of the quinone–phenolate system standing perpendicularly on the rim of a β-CD of the initial encounter complex, leading spontaneously to the lactone structure **I** within the β-CD.

Although it is difficult to specify one particular elementary force that is responsible for the lactonization reaction in a β-CD, one can imagine that the initial penetration of the aryl-residue portion bearing the carboxylate anion into the cavity of a β-CD moiety acts as a trigger for the subsequent events by dragging the two phenolic groups (those to be maintained) onto the β-CD; then the above forces collectively assist the subsequent transformation toward the formation of the lactone dianion **I** by means of close-fitting binding to the β-CD. It should also be noted that the non-bonded repulsive force between PP and the β-CD can largely define the whole conformation of the PP–β-CD complex as currently studied by the optimal space-filling molecular model, and, in this case of a tight binding mode, accompanied by the dominant packing

entropy loss of a red coloured phenolphthalein from its translational, rotational, and vibrational origins once trapped in a β-CD molecule. In other words, the specific binding *per se* provides the driving force to reduce the free energy of activation for the lactonization within a β-CD molecule.

This example of β-CD catalysis of lactonization is especially interesting because of its high specificity and its enormous, diffusion-controlled rate. Catalysis by a similarly complexed α-CD or γ-CD is far less efficient, and far more loosely bound complexes are formed than in the case with which we are mainly concerned with here.

Experimental

Materials.—Disodium salt of phenolphthalein was of commercial origin. Titration with standard hydrochloric acid solution in ethyl alcohol–water mixtures showed 98% (±3%) purity. The pH-reading for 0.1 mol dm^{-3} D_2O solution was recorded as 11.10 and by adding 0.3 units, the apparent pD was determined to be 11.40.

NMR Measurements.—^1H and ^{13}C NMR spectral measurements were performed on a JNM-GSX 270 FTNMR system (JEOL) at 270.05 MHz for ^1H, and at 67.80 MHz for ^{13}C in the Fourier transform mode at a probe temperature of 300 K. The digital resolution was ±0.001 ppm for ^1H with 32 768 data points, and ±0.008 ppm for ^{13}C with 65 536 data points by 24 000 scans.

Although the binding studies in Me_2SO are yet to be completed, the dissociation constant of PP–β-CD complex in Me_2SO was found to be in the neighbourhood of 10^{-5} mol dm^{-3} and, as also seen in the clear and distinct resonance peaks, the NMR spectra showed the tight binding nature of the complex in Me_2SO as well as in aq. solution.

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