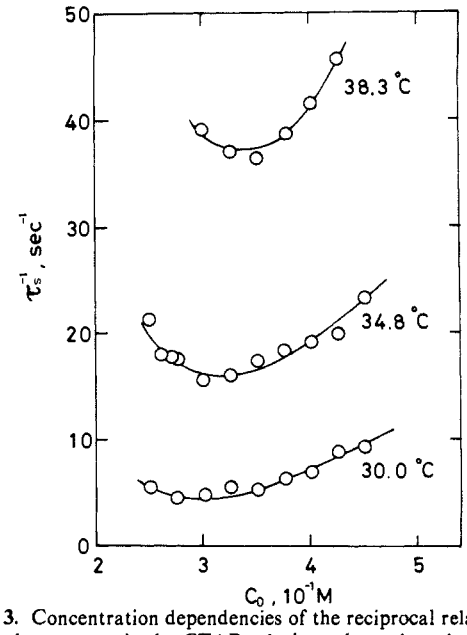
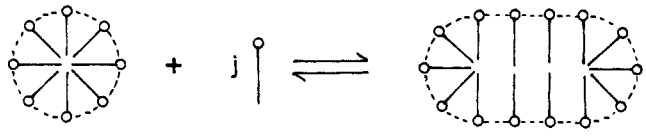


Figure 3. Concentration dependencies of the reciprocal relaxation time for the slow process in the CTAB solutions above the sphere–rod transition concentration at various temperatures.

to a sphere micelle in a similar manner as a sphere micelle is formed, i.e.



(1)

The breaks in the concentration dependencies of conductivity and ultrasonic velocity at the sphere–rod transition concentration were very similar to those at the CMC[6] and support our interpretation. A similar model has been discussed by Mukerjee.[7] Porte et al.[8] also claimed that successive association of the monomers to the sphere micelle leads to a rodlike micelle, energy barrier exists at the first step of elongation, and the elongated micelles with moderate association numbers are energetically disfavored.

For the mechanism of the sphere–rod transition of micelles another conflicting model has been proposed,[9] where a rodlike micelle (S_{mn}) is assumed to be formed by the agglutination of several (n) sphere micelles (S_m), i.e.

$$nS_m \underset{k_b}{\overset{k_f}{\rightleftharpoons}} S_{mn} \tag{2}$$

For reaction 2, the overall concentration of surfactant ($\sum[S]$) and the equilibrium constant (K) is given by

$$\sum[S] = m[S_m] + mn[S_{mn}] \tag{3}$$

$$K = \frac{[S_{mn}]}{[S_m]^n} \tag{4}$$

and the relaxation equation is given by

$$\tau_s^{-1} = n^2 k_f [S_m]^{n-1} + k_b \tag{5}$$

where the brackets indicate the concentration. Since n is estimated to be smaller than five under the present experimental conditions, eq 3 and 4 predict that the increase of $[S_m]$ is convex upward while that of $[S_{mn}]$ is concave upward at around the sphere–rod transition concentration. These facts predict that the solution properties, e.g., conductivity and ultrasonic velocity, vary gradually with surfactant concentration in relatively wide range around the sphere–rod transition concentration. Furthermore, by using the values of n and $[S_m]$ estimated above, eq 5 predicts that τ_s^{-1} increases very steeply with surfactant concentration. However, all these expectations were contradicted to the experimental results as shown in Figures 1 and 3. Then a mechanism of direct agglutination of sphere micelles to form a rodlike micelle was discarded.

Even though further studies are needed to provide quantitative interpretations, we may conclude that the rodlike micelle formation of CTAB occurs via successive association of monomers to the sphere micelle in the time region of several hundred milliseconds, while the monomer exchange on the rodlike micelle occurs in the time range of several milliseconds at 30 °C.

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Solution Study and Molecular Structure of a [3]-Catenand: Intramolecular Interaction between the Two Peripheral Rings

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For many years, topologically novel molecules such as catenanes (interlocked rings) have been the target of synthetic efforts in several laboratories.[1-4] With regard to synthetic efficiency, the copper(I) templated synthesis of catenates (complexes) and catenands (free ligands) appears to be among the most efficient methods.[5] Schill et al. have demonstrated syntheses of [3]-catenanes, consisting of three interlocked rings, by using carbon-based control units.[6] Recently, coordinating systems containing three interlocked macrocyclic subunits have been synthesized.[7,8] The X-ray structure of a dicopper(I) [3]-catenate has also been reported.[9]

In the course of our work,[7] we have prepared the dicopper(I) [3]-catenate $[\mathbf{1}(Cu^I)_2]^{2+}\cdot[BF_4^-]_2$, and we have isolated the copper(I) [2]-catenate $[\mathbf{2}(Cu^I)]^{+}\cdot BF_4^-$ as a byproduct.

The corresponding catenands **1** and **2** (see Figure 1) were readily obtained from their respective copper(I) catenates by demetalation with KCN. Both compounds **1** and **2** have been studied by ^1H NMR, and their conformational properties have been compared in the light of the crystal structure of **1**, determined by X-ray

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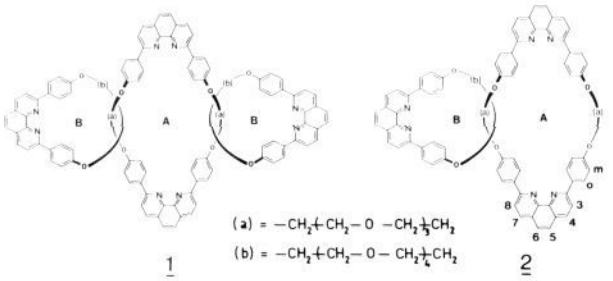

Figure 1.

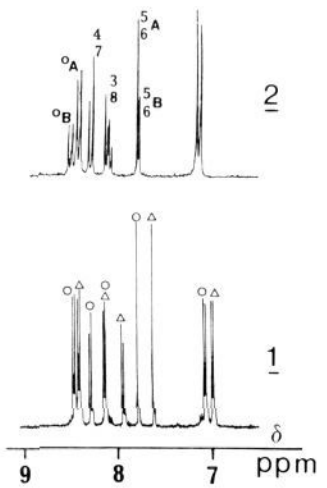

Figure 2. Comparison of the ^1H NMR spectra of **1** and **2**.

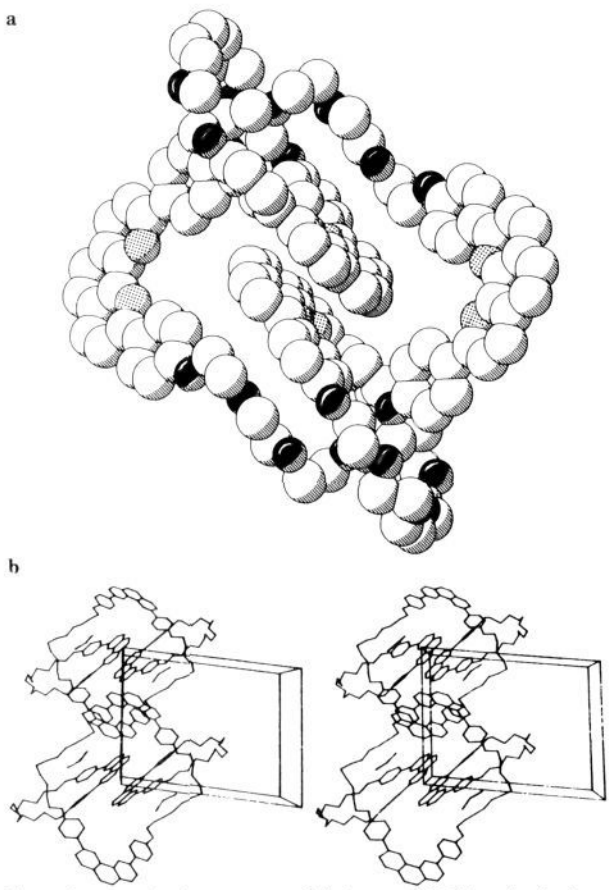

Figure 3. **a**: molecular structure of **1**, the two CH_2Cl_2 molecules have been omitted for clarity. **b**: intermolecular packing within the crystal lattice of **1**, $2CH_2Cl_2$.

diffraction. These results are presented hereafter.

By comparing the ^1H NMR spectra of **1** and **2** (Figure 2) recorded under the same conditions (CD_2Cl_2; 298 K; 400 MHz for **1** and 200 MHz for **2**), it is clear that the solution structures of both compounds display an important difference. For **2**, full assignment of the spectrum could be obtained, the aromatic region being the juxtaposition of the spectra corresponding to two 2,9-diphenyl-1,10-phenanthroline (dpp) subunits, with chemical shifts very similar to those previously observed for other [2]-catenands.[5] Some slight differences can be noticed between the two rings A (54-membered rings) and B (30-membered rings) for the o and m protons. This is in agreement with earlier observations on the influence of the ring size on the ^1H chemical shift.[7,10] On the other hand, the protons $H_{3,8}$, $H_{4,7}$, and $H_{5,6}$ have almost superimposable signals for both types of 1,10-phenanthroline (phen) nuclei (rings A and B), suggesting that the three phen nuclei of **2** are independent in solution and that their chemical environment is the same.

Surprisingly, by going from **2** to **1**, the addition of one 30-membered ring B destroys the similarities between the phen nuclei of A (phen A) and those of B (phen B). In the spectrum of **1**, a significant upfield shift (−0.2 ppm) was observed for one type of dpp (Δ signals), the other pair of dpp fragments (O signals) being almost unaffected ($\Delta\delta < 0.02$ ppm between **1** and **2**). Obviously, this observation suggests that a new type of molecular arrangement is adopted by **1**, although the entwined topography of catenates[4] can be excluded. In view of the relatively important difference between the chemical shifts of both types of phen, it might be postulated that stacking interactions take place between two equivalent phen nuclei, the two other ones being also equivalent and independent. On the ground of ^1H NMR studies only, it is difficult to tell whether the stacking phen nuclei belong to ring A or rings B. The ambiguity was raised by the solid-state structure. Stereo views of the molecular structure of **1** are given on Figure 3. [Crystals of **1** were grown from CH_2Cl_2–toluene. Crystal data: $C_{134}H_{132}N_8O_{22}Cl_2$, triclinic space group $P\bar{1}$, a = 18.564 Å, b = 14.096 Å, c = 11.677 Å, α = 96.49, β = 89.79, and γ = 96.14°, z = 1. The data were collected on a 4-circle diffractometer by using Cu Kα (d = 1.5418 Å) radiation with high speed recording (0.75° s^{-1}). From 11 484 measured reflections, only 2686 were significantly observed to the 3_δ(I) level. The structure was solved by direct methods[11] and refined by the large blocks least-squares method.[12] Partial occupancy factors (0.8/0.2) were used, and constraints to the atom–atom distances[13] were applied except in the last refinement cycle, leading to an R-factor of 11.8%.] The geometry of the system is very particular, the two 30-membered rings (B) being roughly planar and parallel to one another but directed in opposite directions.

The phen units of the two B rings are parallel and stacked with a short interplane distance (3.34 Å). Interestingly, the phen nuclei belonging to the large cycle A undergo intermolecular stacking interactions within the lattice, as shown in Figure 3b. In other words, all the phen rings are stacked, either intra- or intermolecularly.

The cycle A adopts a chair-like conformation, the $-(CH_2CH_2O)_3-$ folds of which forming with the (B) rings two molecular hollows in which CH_2Cl_2 molecules embed themselves. In this way they come to close contact with parts of **1**. The self-organization and the cavity-filling conformation of compound **1** may be related to recent studies which demonstrate similar self-complexation of one aromatic unit in macrocyclic polyethers.[14,15]

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In conclusion, the solution conformation and the molecular structure in the solid state of the [3]-catenand **1** are in good agreement. The geometry of the molecular system (ternary structure) is determined by the formation of optimal intramolecular associations between aromatic subunits, the contribution of intermolecular stacking being also significant in the crystal.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, relevant distances in one whole molecule, and relevant dihedral angles between mean planes (9 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Antibody Catalysis in Reverse Micelles

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Recently, it was demonstrated that the high affinity and specificity of antibodies could be exploited in the design of catalysts for acyl-transfer,[1-3] pericyclic,[4] photochemical,[5] and redox reactions.[6] Because antibodies can be selectively elicited to a vast array of structurally diverse molecules,[7] these experiments offer the possibility of producing tailor-made catalysts for applications in biology, chemistry, and medicine.[8] The versatility of antibody catalysis would be substantially expanded if reactions could also be performed in nearly anhydrous solvents, reverse micelles, or aqueous-organic biphasic systems.

Several low molecular weight proteins have been solubilized in the hydrophilic core of reverse micelles, which are formed when water/surfactant mixtures are dissolved in water-immiscible solvents.[9-11] NMR,[12] CD, and fluorescence[13] studies have demonstrated that these proteins do not undergo major structural changes when solubilized in reverse micelles and kinetic studies reveal that enzymatic activity is also retained.[14] Quasielastic light[15] and small-angle neutron scattering probes[11,16] of reverse micelle structure demonstrated that the radii of reverse micelles are similar to the radius of the enclosed macromolecule. The size of reverse micelles is also controlled by the molar ratio of water to detergent (Wo). Most low molecular weight enzymes display maximal activity at Wo's between 10 and 15,[16] whereas lipoxygenase (100 K daltons) displayed maximal activity at a Wo of 30.[10] There is only one report describing antigen–antibody interactions in reverse micelles,[17] and in that case polyclonal antibodies were used and antibody activity was assessed indirectly. We now report that an antibody generated to the transition-state analogue, phenylphosphonate **1**, catalyzes the hydrolysis of phenylacetate in reverse micelles with rates comparable to those observed in aqueous solutions.

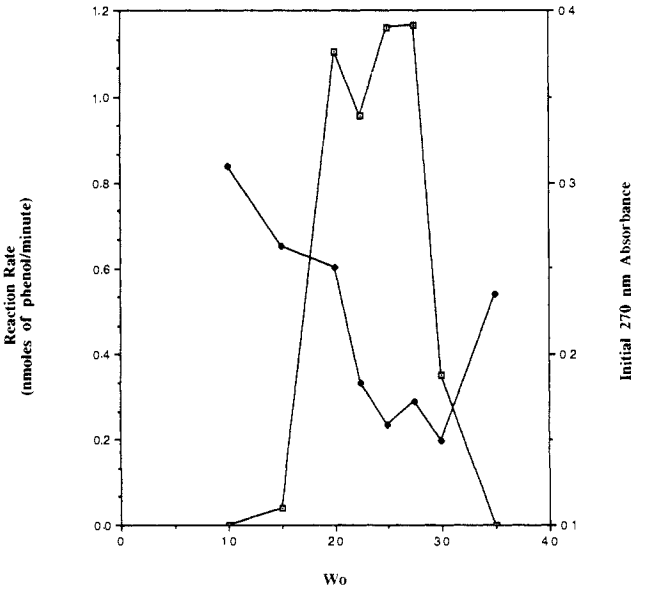
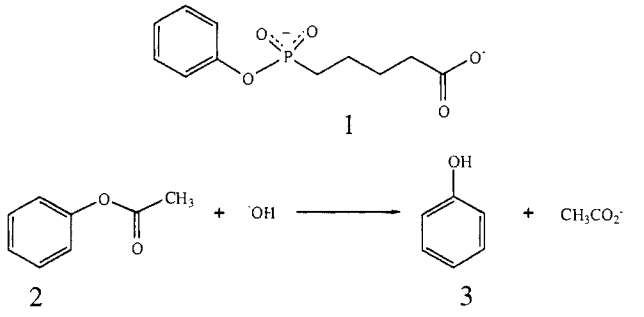


Figure 1. Rate of antibody-catalyzed hydrolysis of phenylacetate in reverse micelles as a function of Wo (□). The extent of forming antibody-containing reverse micelles (i.e., the initial A_{270}) as a function of Wo (◆). Note that the 270-nm absorbance reflects contributions from **2**, protein, and reverse micelle turbidity.

Scheme I



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