approaching the present limitations of the instrumentation (~3000).

Of considerable interest is the ease by which biologically important and chemically unstable surfactants, illustrated here by vitamin K_1 and chlorophyll *b*, may be sampled and analyzed. Such a characterization technique need not be limited to the monolayer model but should be extendable to sampling surfactants constrained at other interfaces modeling biological organization.

Chemical reactions may be monitored by sampling the film at various times. For instance, it is known that chlorophyll loses its magnesium atom to become metal-free pheophytin when brought into contact with aqueous acid. Figure 2 reproduces the original oscillographic tracing of an emitter sampled film of chlorophyll *b*[18] which had been spread ($\Pi \approx 0$ dyn/cm) on an aqueous 10^{-3} M HCl subphase for 10 min (22 °C). While the spectrum of chlorophyll *b* on neutral subphase showed only the molecular ion at mass 907.5 the formation of the metal-free pheophytin *b* (mass 885.5) is clearly demonstrated on aqueous acid. Owing to uncertainties in the mechanism by which ionization and subsequent field desorption take place the observed variation in signal intensity for different compounds, and lack of precision in replicate measurements, this method presently can give only a qualitative indication of the extent of reaction.

With a means to obtain a surfactant's molecular weight added to the other methods of separation and characterization, we are close to realizing as complete an experimental description of the chemistry occurring in films of monomolecular thickness as for reactions occurring in homogeneous solution.

References and Notes

(1) Schulten, H. R.; Beckey, H. D. *Org. Mass Spectrom.* **1972**, *6*, 885.
(2) Kuhn, H.; Möbius, D.; Bücher, H. "Techniques of Chemistry", Weissberger, A., Ed.; Interscience: New York, 1972; Vol I, Part IIIB.
(3) Whitten, D. G.; Hopf, F. R.; Quina, F. H.; Sprintschnik, G.; Sprintschnik, H. W. *Pure Appl. Chem.* **1977**, *49*, 379.
(4) Rosilio, C.; Ruaudel-Teixier, A. *J. Polym. Sci., Part A-1* **1975**, *13*, 2459.
(5) Letts, S. A.; Fort, T., Jr.; Lando, J. B. *J. Colloid Sci.* **1976**, *56*, 64.
(6) Enkelmann, V.; Lando, J. B. *J. Polym. Sci., Part A-1* **1977**, *15*, 1843.
(7) (a) Valenty, S. J. *Macromolecules* **1978**, *11*, 1221. (b) Richard, M. A.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 6613.
(8) Gaines, G. L., Jr.; Behnken, P. E.; Valenty, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 6549.
(9) Valenty, S. J. *J. Am. Chem. Soc.*, **1979**, *101*, 1.
(10) Schulten, H.-R. "Methods of Biochemical Analysis", Glick, David, Ed.; Wiley: New York, 1977; Vol. 24, pp 313–448.
(11) The preparation and characterization of 1 are found in ref 12.
(12) Valenty, S. J.: Behnken, P. E.; Gaines, G. L. Jr. *J. Am. Chem. Soc.*, submitted for publication.
(13) Bikerman, J. J. *Proc. R. Soc. London, Ser. A* **1939**, *170*, 130.
(14) Calculated as described in ref 15.
(15) Olson, K. L.; Cook, J. C.; Rinehart, K. L., Jr. *Biomed. Mass Spectrom.* **1974**, *1*, 358.
(16) Valenty, S. J., 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 1978; American Chemical Society: Washington, D.C.; COLL 081; *Adv. Chem. Ser.*, in press.
(17) Ligon, W. V. Jr. *Science*, in press.
(18) The application of FD MS to the analysis of porphine compounds has been described by Evans et al.[19]
(19) Evans, N; Games, D. E.; Jackson, A. H.; Matlin, S. A. *J. Chromatogr.* **1975**, *115*, 325.

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Duplex Cyclodextrin

Sir:

During the past decade, the basic characteristics of enzymes such as saturation kinetics or large catalytic constants have been successfully modeled not only by the use of naturally occurring compounds[1] but also by the construction of partially[2] or completely[3] artificial molecules of appropriate shape and necessary functionalization. A remarkable strengthening of the hydrophobic binding was also achieved on increasing the area of the hydrophobic recognition site of a host molecule.[4,5] The observation that the introduction of a second (appropriate) recognition element ("double recognition" [6]) onto the host molecules mentioned above afforded a significant increase in binding gave rise to a new strategy for the modeling of more complex and sophisticated enzyme functions (Figure 1).

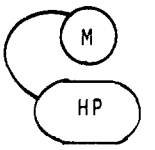

Figure 1. Double recognition:[6] M acts as a coordination binding site and/or a catalytic site.

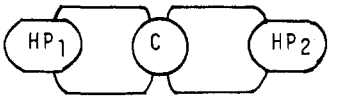

Figure 2. Triple recognition for ligase-type activity: HP_1, HP_2, hydrophobic binding sites; C, another recognition element (acid, base, metal, etc.).

In order to construct better enzyme models, a more precise (synthetic) recognition system is required. Triple recognition, for example, should be the minimal condition necessary for modeling a ligase-type activity (to show specificity toward both S_1 and S_2 as well as toward the functional group(s) F_1 and F_2 in eq 1). In this communication, the authors report that a novel host molecule, **duplex cyclodextrin,** which has two hydrophobic binding sites (HP_1 and HP_2 in Figure 2) together with another recognition element C, does specifically bind methyl orange, a guest dye molecule having two hydrophobic recognition elements. Thus, capped β-cyclodextrin (**1**)[5a] was converted to di(ω-aminoethylamino)-β-cyclodextrin (**2**) in 80% yield on heating in a large excess of ethylenediamine at 50 °C for 3 h.

$$S_1\text{-}F_1 + F_2\text{-}S_2 \rightarrow S_1\text{-}F_{1,2}\text{-}S_2 \qquad (1)$$

The tetramine treated with a slight excess of **1** in DMF–pyridine (1:1 by volume) at 80 °C for 72 h gave **duplex β-cyclodextrin (3)** (Scheme I) in 16% yield.[7] Purification of **2** or **3** was achieved by the ion-exchange column chromatography through anion- (IR-45) and cation- (Dowex-50W) exchange resins followed by microcrystalline cellulose column chromatography.

A paper chromatogram (7% NH_4OH–EtOH–BuOH, 5:5:1) of **3** thus purified exhibited a clear single spot of R_f 0.6 (ninhydrin). The elemental analysis of **3** was satisfactory, although

Scheme I

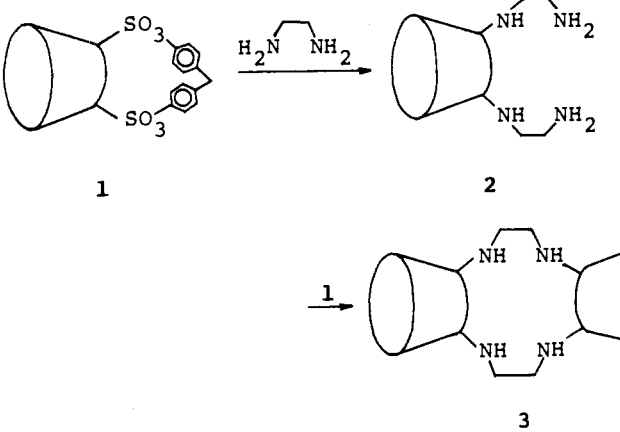

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Table I. ^{13}C NMR Chemical Shift in D_2O[a]

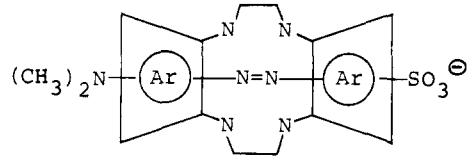
compd	^{13}C chemical shift, ppm
2	100.06 (C_1), 79.35 (C_4), 71.23 (C_3), 70.19 (C_2, C_5), 58.70 (C_6), 45.45 (C-NHR), 37.08 (C-NH_2)
3	100.45 (C_1), 79.66 (C_4), 71.75 (C_3), 70.39 (C_2, C_5), 58.77 (C_6), 47.66 (C-NHR)
$(CH_3CH_2)_2NH$[b]	44.1 (C-NH-C)
$CH_3CH_2NH_2$[c]	35.9 (C-NH_2)

[a] Acetone was used as an internal standard. [b] L. F. Johnson and W. C. Hankowski, "Carbon-13 Spectra", Wiley-Interscience, New York, 1972. [c] E. Breitmaier, G. Haas, and W. Voelter, "Atlas of Carbon-13 NMR Data", Plenum Press, New York, 1976.

solvent molecule(s) was usually bound much tighter than by parent cyclodextrin. Found: C, 45.21; H, 6.53; N, 3.02. Calcd for $C_{88}H_{148}N_4O_{66}\cdot(CH_3)_2NCHO$: C, 45.69; H, 6.54; N, 2.93. Calcd for $C_{88}H_{148}N_4O_{66}$: C, 45.58; H, 6.44; N, 2.42.

The NMR spectra of both **2** and **3** show the characteristic absorptions of the protons α to amino nitrogen at δ 3.4 in D_2O: **2**, δ 3.4 (12 H, N-CH_2), 3.7–4.9 (38 H), 5.4 (7 H, C_1 H); **3**, δ 3.4 (16 H, N-CH_2), 3.6–4.8 (76 H), 5.4 (14 H, C_1 H). More characteristic are the ^{13}C NMR spectra of **2** and **3**; the former, as listed in Table I, shows two types of methylene absorption adjacent to the primary and secondary amino groups while no methylene absorption adjacent to the primary amino group is observed in duplex cyclodextrin (**3**).

The present host duplex cyclodextrin shows unique and interesting binding characteristics toward guest molecules having two hydrophobic recognition sites. One typical example of this multiple recognition is the binding of 6-*p*-toluidinylnaphthalene-2-sulfonate (TNS) where its fluorescence maximum at 480 nm in aqueous solution[8] shifted to 444 nm in the presence of duplex cyclodextrin. This large shift due to the hydrophobic environment of the host–guest inclusion complex is approximately equal to that of 2:1 β-cyclodextrin–TNS complex but much larger than that of the corresponding 1:1 complex as the following data suggest: aqueous, 480; β-duplex 1:1 complex, 444; β-CD 1:1 complex, 457; β-CD 2:1 complex, 444; β-CD$(N_2C_2H_6)_2$ (**2**) 1:1 complex, 452 nm. This suggests that the binding of TNS by duplex cyclodextrin is very similar to that involved in 2:1 β-CD inclusion. Another example is binding of methyl orange where the association constant with duplex cyclodextrin was 3160 M^{-1}, much higher than that with the corresponding β-CD tetramine **2** (520 M^{-1}), demonstrating the additive contribution of the second hydrophobic binding site.[9] These examples strongly support the multiple recognition mechanism for binding by duplex cyclodextrin as shown in **4**.



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References and Notes

(1) (a) F. Cramer and W. Kampe, *J. Am. Chem. Soc.*, **87**, 1115 (1965); (b) R. L. van Etten, J. F. Sebastian, G. A. Clowes, and M. L. Bender, *ibid.*, **89**, 3242 (1967); (c) D. L. Vander Jagt, F. L. Killian, and M. L. Bender, *ibid.*, **92**, 1016 (1970); (d) T. S. Straub and M. L. Bender, *ibid.*, **94**, 8875, 8881 (1972); (e) R. Breslow and P. Cambell, *Bioorg. Chem.*, 1, 140, (1971); (f) I. Tabushi, K. Fujita, and H. Kawakubo, *J. Am. Chem. Soc.*, **99**, 6456 (1977).

(2) (a) F. Cramer and G. Mackenson, *Angew. Chem.*, **78**, 641 (1966); (b) F. Cramer and G. Mackenson, *Chem. Ber.*, **103**, 2138 (1970); (c) R. Breslow and L. E. Overmann, *J. Am. Chem. Soc.*, **92**, 1075 (1970); (d) W. B. Gruhn and M. L. Bender, *Bioorg. Chem.*, **4**, 219, 237 (1975); (e) R. Breslow, J. B. Doherty, G. Guillot, and C. Lipsey, *J. Am. Chem. Soc.*, **100**, 3227 (1978).

(3) (a) I. Tabushi, Y. Kuroda, and Y. Kimura, *Tetrahedron Lett.*, 3327 (1976); (b) I. Tabushi, H. Sasaki, and Y. Kuroda, *J. Am. Chem. Soc.*, **98**, 5727 (1976); (c) I. Tabushi, Y. Kimura, and K. Yamamura, *ibid.*, **100**, 1304 (1978).

(4) J. Emert and R. Breslow, *J. Am. Chem. Soc.*, **67**, 670 (1975).

(5) (a) I. Tabushi, K. Shimokawa, N. Shimizu, H. Shirakata, and K. Fujita, *J. Am. Chem. Soc.*, **98**, 7855 (1976); (b) I. Tabushi, K. Shimokawa, and K. Fujita, *Tetrahedron Lett.*, 1527 (1977); (c) I. Tabushi, L. C. Yuan, and K. Fujita, *ibid.*, 2503 (1977).

(6) I, Tabushi, N. Shimizu, T. Sugimoto, M, Shiozuka, and K. Yamamura, *J. Am. Chem. Soc.*, **99**, 7100 (1977).

(7) The ^{13}C NMR spectrum of 1 supports the assignment of the disulfonyl group capping positions as the remote transannular ones (6A,6C and/or 6A,6D). See ref 2e. We have also observed the same ^{13}C NMR for 1. Therefore, if 1 is the mixture of 6A,6C and 6A,6D, six possible isomers of present duplex cyclodextrin should exist:

$$\binom{6A,6C}{6A,6C},\ \binom{6A,6C}{6C,6A},\ \binom{6A,6C}{6A,6D},\ \binom{6A,6C}{6D,6A},\ \binom{6A,6D}{6A,6D},\ \binom{6A,6D}{6D,6A}$$

(8) Since no fluorescence of TNS could be observed in pure water, the fluorescence maximum of free TNS employed here was measured in 10% ethanol solution.

(9) Most probably a part of the favorable interaction (such as the van der Waals interaction or the loss of water structure) is partially offset by a considerable loss of freedom of motion of the guest molecule in the duplex inclusion complex. Cf. I. Tabushi, Y. Kiyosuke, T. Sugimoto, and K. Yamamura, *J. Am. Chem. Soc.*, **100**, 916 (1978).

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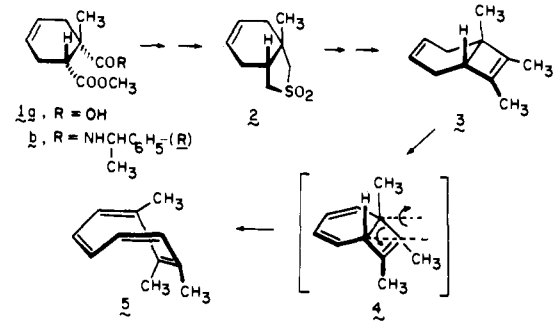
Bond Fixation in Annulenes. 5. Absolute Configuration and Chiroptical Properties of Optically Active 1,2,3-Trimethyl- and 1,2,3,4-Tetramethylcyclooctatetraenes[1]

Sir:

Whereas the smaller annulene ring systems (cyclobutadiene and benzene) are too planar to support optical activity[2] and the larger annulenes are too flexible to maintain chirality,[3] the medium-sized cyclooctatetraene nucleus is ideally suited for probing the interaction of light with a cyclic conjugated polyolefin network. The successful realization of this objective is dependent upon adequate inhibition of the high susceptibility of these tub-shaped molecules toward ring inversion and π-bond alternation,[4] processes which normally result in facile racemization. The control of these dynamic phenomena having been mastered,[1,5-7] we can now report the first absolute configurational assignments to two chiral [8]annulene hydrocarbons and the elucidation of their chiroptical properties.

The assignment of absolute stereochemistry to (−)-**5** began by sequential reaction of fully resolved acid ester **1a**, $[\alpha]^{25}_D$ −13.8° (*c* 10.8, C_2H_5OH),[1] with oxalyl chloride and excess (*R*)-(+)-α-methylbenzylamine to give **1b**, mp 95–97 °C, $[\alpha]^{25}_D$ + 66.5° (*c* 18.8, C_2H_5OH).[8] This compound was isolated as monoclinic crystals of space group $P2_1$ with lattice constants a = 10.084 (3), b = 9.429 (3), c = 18.234 (4) Å; β = 96.36 (2)°. An observed and calculated density of ~1.16 g/cm^3 indicated four molecules in the unit cell or two molecules of composition $C_{18}H_{23}NO_3$ in the asymmetric unit. All unique diffraction maxima with $\theta \leq 57°$ were collected (Cu



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