to the difference between their average orientational parameters in the chiral medium.

The effect described here opens up a new and very wide field in the study of the geometry of chiral molecules through their dipolar spectra. Furthermore, following the work of Solladié et al.[9] regarding the sign of the pitch induced by a chiral molecule, it could be possible to relate the orientational parameters to the absolute configuration of the enantiomers in a given homologous compound series.

A systematic study is underway in our laboratory to optimize the different parameters such as temperature, relative concentration, and nature of the nematic and the cholesterogenic compounds as well as other NMR experimental conditions. On a more theoretical point of view, we are analyzing the effect of the pitch and the elastic constants of the twist[10] in these mixtures in order to be able to account for their interesting behavior in a magnetic field. There certainly exist other potential applications for these macroscopically, easily orientated cholesteric phases, to name a few—color display, light modulator in the visible and near-infrared range, etc.

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Very Strong Binding of Appropriate Substrates by Cyclodextrin Dimers

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Received June 8, 1989

With the best substrates, a well-fitting cyclodextrin can achieve a binding constant, in water, of ca. 10^4 M^{-1}; this is not as strong as some enzymes and most antibodies, which typically bind several substrate segments. Many years ago we prepared dimeric cyclodextrin[1] **1**; other linked cyclodextrin dimers have also been made.[2] Recently dimer **2** has been reported,[3] and the finding that it shows reasonably strong (2×10^6 M^{-1}) binding of ethyl orange. However, only one segment of ethyl orange is significantly hydrophobic. We find that with substrates bearing two real hydrophobic segments the binding by dimeric cyclodextrins can be very strong.

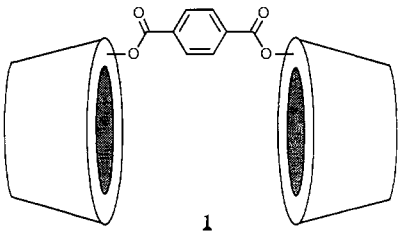
As binding hosts we examined dimers **2-4**. Compound **3** was prepared by opening our β-cyclodextrin 2,3-mannoepoxide[4] with benzyl mercaptan, then reduction (Na, NH_3) to the thiol, and air oxidation to the disulfide **3**.[5] It is thus the 2-epihydroxy 3-epidisulfide. It showed the expected ^{1}H NMR spectrum and a *m/e* (FAB) of 2323 (M + Na). Compound **4** was prepared by acylation of β-cyclodextrin at C-6 with thioxanthone-3,6-dicarbonyl dichloride. After purification by reverse-phase chromatography, it showed the expected ratios of aromatic and anomeric protons in the 400-MHz ^{1}H NMR spectrum.

We examined compounds **5-16**[6] as guests. Binding into the hosts led to an observable change in circular dichroism (CD), used to determine binding constants. Sometimes competition studies were used to establish or confirm binding constants. We have also synthesized BNS[7] (**17**),[8] an analogue of ANS that binds strongly to **2**, producing a fluorescent complex. Some binding constants were established by competition of **17** with other guests for binding into **2**.

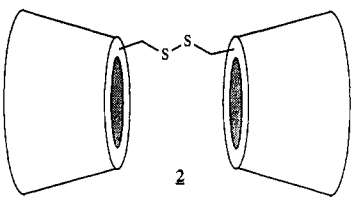
Table I. Binding Constants (25 °C)

guest	solvent	K_a,[a] M^{-1}
	To Host **2**	
acetylene **5**	glycol	$9 \pm 2 \times 10^3$
trans-stilbene **7**	glycol	$2 \pm 1 \times 10^4$
ester **8**	glycol	$1.3 \pm 0.01 \times 10^4$
dihydrostilbene **10**	glycol	1×10^4[b]
N-methylamide **15**	glycol	$9 \pm 3 \times 10^3$
cis-stilbene **6**	H_2O	$<3 \times 10^3$
ester **8**	H_2O	$1 \pm 0.8 \times 10^8$
amide **9**	H_2O	$2.4 \pm 0.4 \times 10^4$
disulfide **11**	H_2O	$1 \pm 0.3 \times 10^6$
fumarate **12**	H_2O	$<3 \times 10^3$
cyclopropene **13**	H_2O	3.5×10^8[c]
cyclopropane **14**	H_2O	1×10^8[c]
p-tert-butylphenol (**16**)	H_2O	$1.6 \pm 0.4 \times 10^4$
BNS (**17**)	H_2O	5×10^6[d]
	To Host **4**	
cyclopropene **13**	glycol	1.3×10^5
cyclopropene **13**	H_2O	7.0×10^8[e]

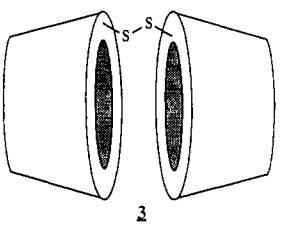
[a] From the change in circular dichroism intensity with varying concentrations of the guest, except where noted. [b] By competition with **5**, whose induced circular dichroism is significant. [c] By competition with the fluorescent guest **17**. [d] From the change in fluorescence intensity with varying concentrations of the host. [e] By competition with host **2** for the guest.



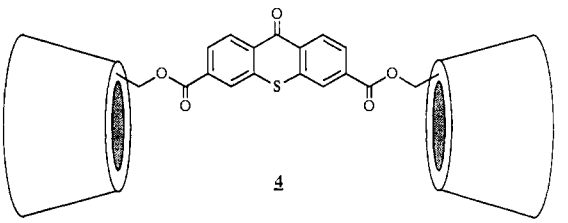
1



2



3



4

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(2) (a) Harada, A.; Furue, M.; Nozakura, S.-I. *Polym. J.* **1980**, *12*, 29. (b) Tabushi, I.; Kuroda, Y.; Shimokawa, K. *J. Am. Chem. Soc.* **1979**, *101*, 1614. (c) Fujita, K.; Ejima, S.; Imoto, T. *Chem. Lett.* **1985**, 11.
(3) Fujita, K.; Ejima, S.; Imoto, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1277.
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(5) This compound was first prepared in our laboratories by Dr. Albrecht Berkessel.
(6) All were characterized by ^{1}H NMR and MS. The syntheses are straightforward; the cyclopropene and cyclopropane were prepared by reaction of ethyl diazoacetate with the appropriate acetylene or olefin.

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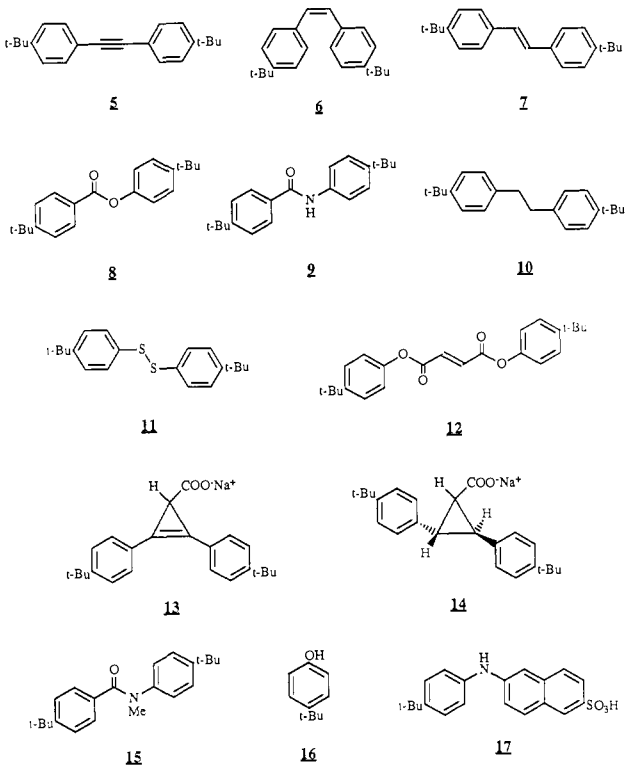
Chart I



Ethylene glycol was sometimes used to weaken the binding (*m-t*-butylphenyl acetate binds to β-cyclodextrin ca. 150 times more weakly in ethylene glycol than in water). As Table I shows, ester **8** and cyclopropene **13** are very strongly bound to **2**, with constants (water) exceeding 10^8 M^{-1}. Interestingly, amide **9** is considerably weaker and the disulfide **11** is somewhat weaker, while the overlong fumarate ester **12** and the crowded *cis*-stilbene **6** (but cf. the slightly less crowded cyclopropene derivative **13**) are only weakly bound.

In ethylene glycol solvent (Table I), the ester **8** is now a little over 10^4 times more weakly bound than in water, almost exactly what would be predicted for two *tert*-butylphenyl groups with this solvent change. The *trans*-stilbene **7**, the dihydrostilbene **10**, and the diarylacetylene **5** are comparable to the ester **8**, as is the *N*-methylamide **15**.

The diester **4** binds monodentate substrates with a normal ca. 10^4 M^{-1} constant but the bidentate cyclopropene substrate **13** quite strongly, twice as well (by direct competition) as does the dimer **2**. The secondary disulfide dimer **3**, by contrast, showed no enhanced binding; apparently the tight linkage crowds the system unduly.

Our largest binding constants of 10^8–10^9 are already similar to those of medium-affinity antibodies. With more rigid links between the cyclodextrins, the binding constants should be even higher. Dimer **4** carries a catalytic group that can direct chlorination.[10] Thus the potential for the use of such multiple binding in enzyme mimics seems very attractive.

Acknowledgment. Support of this work by the NIH and the ONR and a Chaim Weizmann Postdoctoral Fellowship to N.G. from the American Committee for the Weizmann Institute of Science are gratefully acknowledged.

(7) We propose this acronym for 2-(*p-tert*-butylanilino)naphthalene-6-sulfonic acid. The compound is fluorescent when bound to a cyclodextrin, but not when unbound in solution.

(8) Prepared from 2-aminonaphthalene-6-sulfonic acid and *p-tert*-butylaniline under the Bucherer conditions used by Kosower[9] to synthesize analogous ANS derivatives.

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Ethynol: A Theoretical Prediction of Remarkably High Gas-Phase Acidity

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Received April 26, 1989

In a recent communication that describes the first generation and direct observation of an ynol in solution,[1-3] Kresge, Wirz, and co-workers[1] noted that phenylynol (PhC≡COH) is more acidic than its enol analogue, PhCH=CHOH, by at least 7 pK_a units. This is a striking result and raises some interesting questions. One immediate point of interest is whether or not this result carries over to the gas phase, i.e., is it an intrinsic effect or is it a solvent effect?[4] A second point of interest concerns the origin of the high relative acidity of the ynol: is it largely due to some special stability of the ynolate anion or to some special instability of the neutral ynol? In order to address these questions, we have carried out ab initio molecular orbital calculations of the gas-phase acidities of the prototype enol (CH_2=CHOH) and ynol (HC≡COH) and related systems.

Standard ab initio molecular orbital calculations[5] were carried out with a modified version[6] of the Gaussian 86 system of programs.[7] Geometry optimizations were performed for all systems at the HF/6-31+G* level and improved relative energies obtained from MP4/6-311+G** calculations at these optimized geometries. Zero-point vibrational contributions to the relative energies were obtained from HF/6-31+G* vibrational frequencies, scaled by 0.9. Relevant energy data are presented in Table I and Figure 1.[8]

We begin our discussion by comparing several of the quantities that we have calculated with experimental or theoretical data from the literature. Our calculated energy difference between vinyl alcohol and acetaldehyde of 56 kJ mol^{-1} (Table I, reaction 1) is somewhat higher than a previous lower level theoretical value[9] of 45 kJ mol^{-1} and an experimental estimate[10] of 41 ± 8 kJ mol^{-1}. As far as we are aware, there is no experimental value for the energy difference between ethynol and ketene. We calculate a value of 155 kJ mol^{-1}, quite close to a previous lower level theoretical estimate (152 kJ mol^{-1}),[3] confirming that the ynol–ketene energy difference is significantly greater than the enol–keto energy

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(10) (a) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648. (b) We note that, for the related pair of keto–enol systems, acetone and its enol (CH_2=C(CH_3)OH), two separate experiments yielded an energy difference of 58 ± 8 kJ mol^{-1}. See ref 10a and the following: Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4845.

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