

ment to give the crude synthetic product. The HPLC profile for the crude products is shown in Figure 1. The mixed oligonucleotide was found to have a longer retention time (t_R 13.5 min) than the corresponding all-ribonucleotide sequence (t_R 11.5 min) prepared by following standard RNA synthesis procedures.^{4a}

The mixed oligomer was fully characterized by gel electrophoresis⁸ (Figure 2a) and the RNA gel-sequencing technique⁹ (Figure 2b) and compared to the corresponding RNA sequence. Comparison of the sequences in Figure 2b shows the absence of ribo C in the mixed 14-mer. Several 35-unit hybrid DNA-RNA oligomers related to the sequence of the self-cleaving ribozyme⁶ were prepared (2, 3, 4, Table I) and their sequences established.

In conclusion, the procedure described herein allows the facile preparation of heretofore unavailable (deoxy)ribonucleotide polymers. Several of these synthetic polymers related to the sequence of the ribozyme and its substrate have been made and are currently being used to probe the mechanism of RNA catalysis.¹⁰

Acknowledgment. We thank Applied Biosystems for providing the 380B DNA synthesizer. We are also indebted to NSERC (K.K.O.) and MRC (R.J.C.) of Canada for financial support.

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New Approach to Mesophase Stabilization through Hydrogen-Bonding Molecular Interactions in Binary Mixtures

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We report a new approach to novel liquid crystalline moieties having a greatly enhanced mesomorphic range through the formation of intermolecular hydrogen bonds between two dissimilar mesogens.

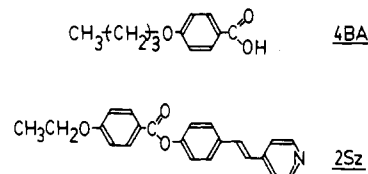
Intermolecular interactions contribute greatly to the formation of molecular aggregates. In liquid crystals, mesomorphicity¹ results from a proper combination of the shape of a molecule and the magnitude and direction of molecular interactions between molecules. While the importance of dipole-dipole interactions in the formation of mesophases has long been established, we have hypothesized that the occurrence of intermolecular hydrogen bonding should have great potential for ordering thermotropic liquid crystals because H-bonding is much stronger than dipole-dipole interactions. However, with some notable exceptions described below, this approach to mesophase formation has remained unsuccessful as, in most cases, the magnitude and direction of H-bonded interactions are not appropriate to keep the fluid state ordered.

A survey of the literature shows that a few monosaccharides^{2,3} and aromatic acid derivatives⁴ show mesophase formation because of the existence of a stable dimer formed through hydrogen bonding. In all of these cases, the compounds always exist as

symmetrical dimers in both their crystalline and mesophase states and the dimer itself may be considered as a single component.

Our approach has been to build a new liquid crystalline system through intermolecular hydrogen bonding between two *different* and *independent* components. The mixing of H-bond donor and acceptor moieties can be expected to form a liquid crystalline hydrogen-bonded complex if the structure is designed properly.

In the present study, 4-butoxybenzoic acid (**4BA**) (nematic from



147 to 160 °C) and *trans*-4-[(4-ethoxybenzoyl)oxy]-4'-stilbazole (**2Sz**), containing a 4-pyridyl group^{5,6} (nematic from 165 to 213 °C) at the extremity of its mesogen, have been selected as H-bond donor and acceptor moieties, respectively. These two molecules have the appropriate structure to form a hydrogen-bonded complex with an overall molecular geometry directed along the long axis of the individual rodlike molecules. In particular, the lone pair of the 4'-pyridyl group of **2Sz** is directed along the molecular axis of the mesogen.

In order to break the self hydrogen bonding of the 4-butoxybenzoic acid dimer units, the complex resulting from an equimolar binary mixture of **4BA** and **2Sz** was prepared by slow evaporation of the mixture from pyridine solution.⁷ The binary complex that was obtained showed an exceedingly stable mesophase as confirmed by differential scanning calorimetry (DSC) (Mettler DSC 30) and by hot-stage polarizing microscopy (Mettler FP 82).

The DSC data shown in Figure 1 (curve B) features endothermic peaks at 136 and 238 °C corresponding respectively to melting (T_m) and isotropization (T_i) transitions for the 1:1 mixture. The isotropization temperature deviated noticeably in the positive direction, and the mesomorphic range ($T_i - T_m$) of the mixture was extended to 102 °C as compared to 13 °C for **4BA** (curve C) and 48 °C for **2Sz** (curve A). Moreover, for the 1:1 mixture, a smectic phase which did not appear for either single component existed between 136 and 160 °C as confirmed by our observation of a focal conic texture under a polarizing microscope. However, this transition was not apparent in our DSC thermogram, and this smectic phase has not yet been classified. The subsequent nematic phase was stable up to 238 °C.

We attribute this unusually strong stabilization of the mesophase of the 1:1 mixture to the *formation of a new and extended mesogen obtained through intermolecular hydrogen bonding* which allows the 1:1 complex to behave as a *single* liquid crystalline component as shown in Figure 2. This is supported by FT-IR measurements which strongly suggest that the acid dimer of **4BA** is replaced by the 1:1 complex. If a simple 1:1 *mechanical* mixture of **4BA** and **2Sz** is prepared, a band at 1681 cm^{-1} due to the carbonyl group of the carboxylic acid dimer ($\text{C}=\text{O}\cdots\text{HO}-$) of **4BA** is observed. In contrast, measurements on the 1:1 molecular mixture prepared from pyridine solution show a new band at 1704 cm^{-1} replacing the band at 1681 cm^{-1} and indicating the existence of the free carbonyl group of the carboxylic acid complexed with the pyridine

(5) **2Sz** was prepared from *p*-ethoxybenzoyl chloride and *trans*-4-hydroxy-4'-stilbazole obtained according to the method of Chiang: Chiang, M.-C.; Hartung, W. H. *J. Org. Chem.* **1945**, *10*, 21-25. Analogous compounds were reported by Nash et al.: Nash, J. A.; Gray, G. W. *Mol. Cryst. Liq. Cryst.* **1974**, *25*, 299-321.

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(7) This method has been used successfully by our laboratory in previous experiments for the formation of homogeneous polymer blends with H-bonding donor and acceptor polymers such as poly(4-hydroxystyrene) or poly(4-vinylbenzoic acid) with poly(4-vinylpyridine). These polymer blends were compatible and showed a single T_i because of the formation of the H-bonded complex: Vivas de Meftahi, M.; Fréchet, J. M. J. *Polymer* **1988**, *29*, 477-482.

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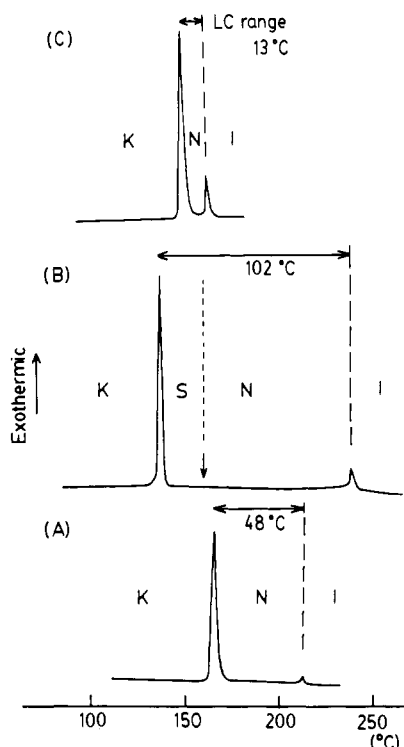


Figure 1. DSC thermograms of (A) **2Sz**; (B) the 1:1 complex of **2Sz** and **4BA** (an arrow indicates the nematic to smectic transition); and (C) **4BA** on heating.

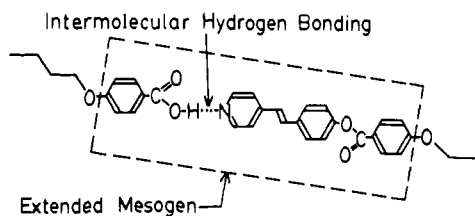


Figure 2. The proposed structure of the new mesogen formed by intermolecular H bonding between **4BA** and **2Sz**.

ring. The sharp melting transition peak of DSC also suggests the existence of a 1:1 complex between **4BA** and **2Sz**.⁸

Coleman et al.⁹ have reported that hydrogen bonding between the pyridine rings and carboxylic moieties was preferred over that between two carboxylic acid units in blends of poly(ethylene-co-methacrylic acid) and poly(2-vinylpyridine). We have also observed a similar behavior in blends of poly(4-vinylbenzoic acid) and poly(4-vinylpyridine); our observation¹⁰ that a 1:1 blend of these two polymers has a glass transition temperature $T_g = 233$ °C, which is 30 °C higher than the calculated weight average T_g , also supports the existence of a strong hydrogen bond between pyridine and carboxylic acid moieties. Further support for the preferred formation of N...HO hydrogen bonds between carboxylic acids and amines can be found in X-ray studies of compounds such as nicotinic acid.¹¹

It is worthwhile noting that, in our system, a single H bond is sufficient to preserve the linearity of the new extended mesogen, in contrast to the two H bonds that were required in the case of the dimeric monosaccharides^{2,3} and aromatic acid⁴ dimers.

(8) A referee has kindly pointed out that the H bonding of the system may be dynamic. At the present time, our data does not allow us to either endorse or reject this suggestion; X-ray experiments in progress only show that the 1:1 complex is favored in the crystalline state.

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The Stereochemistry of the 1,4-Addition of Dibromocarbene to 1,2-Dimethylenecycloheptane

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The 1,4-addition of carbenes to 1,3-dienes has a long and controversial history.¹ Only in recent years, and in rather specific constellations, a number of apparently genuine examples of this reaction have been reported.² In these cases, arguments for a concerted pathway have been presented but alternative, stepwise sequences cannot yet be excluded with the desired degree of certainty. We now wish to report stereochemical evidence supporting a concerted, one-step course of the reaction.

Theory predicts that if this reaction is concerted and controlled by orbital symmetry, it must occur in a disrotatory fashion if it is a linear process and conrotatory for a nonlinear process.³ A suitable 1,3-diene for the investigation of this aspect is (*Z,Z*)-[1',2'-*D*₂]-1,2-dimethylenecycloheptane (**2**) which we have synthesized from the zirconacycle **1**⁴ by stereospecific cleavage of the zirconium-carbon bonds with deuteriosulfuric acid (17 equiv, room temperature, immediate workup), followed by stereospecific removal of the trimethylsilyl groups by treatment with trifluoroacetic acid (2 equiv) in methylene chloride for 10 min (Scheme I). The isotopic and configurational integrity of **2** was proven by ¹H NMR and mass spectroscopy.⁵

The reaction of **2** with dibromocarbene (from bromoform and potassium *tert*-butoxide in pentane at room temperature) yielded the expected^{2e} 9:1 mixture of the 1,2-adduct **3** and the 1,4-adduct **4** in 80% total yield; note that it has previously been shown that there is no secondary rearrangement of **3** to **4**.^{2e} ¹H NMR spectroscopy of **4** does not allow a distinction between the two stereoisomers **4a** and **4b** as both have only one kind of the allylic protons H(8,10); they appear as a broad singlet at $\delta = 3.50$ ppm. Therefore, the mixture of **3** and **4** was reduced with 1 equiv of triphenyltin hydride to give a mixture of stereoisomers of **5** and **6** (Scheme I) which was separated by preparative gas chromatography and investigated by 400 MHz ¹H NMR spectroscopy; the region of the diagnostic bishomoallylic proton H(9) of **6** is presented in Figure 1a. In principle, **6** might consist of three stereoisomers: **6a** (derived from the conrotatory adduct **4a**) and

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(5) **2**: ¹H NMR (90 MHz, CDCl₃) $\delta = 4.74$ (br s, 2 H), 2.35 (m, 4 H), 1.60 (m, 6 H); MS *m/z* (rel intensity) 124 (43), M⁺. Both spectra indicated a D₂-incorporation of approximately 95%. 1,2-Dimethylenecycloheptane:⁶ ¹H NMR (90 MHz, CDCl₃) $\delta = 5.14$ (m, 2 H), 4.73 (m, 2 H), 2.33 (m, 4 H), 1.60 (m, 6 H). **6b** + **6c** (1:1): ¹H NMR (400.1 MHz, CDCl₃, 296 K) **6b** $\delta = 4.47$ (t of quintet, ³J_{HH} = 4.0 Hz, ³J_{HD} = 1.0 Hz, 2 H, H(9)), 2.75 (m, 2 H, H(8)/H(10)), 2.08 (m, 4 H), 1.62 (m, 6 H); **6c** $\delta = 4.48$ (br t, ³J_{HH} = 7.2 Hz, 2 H, H(9)), 2.97 (m, 2 H, H(8)/H(10)), 2.08 (m, 4 H), 1.62 (m, 6 H). MS *m/z* (rel intensity) 216 (6, with isotope pattern), M⁺. D-incorporation (estimated by comparison of the HRMS spectrum of **6b/6c** with that of the unlabeled parent **6H**) 90.6% D₂, 5.9% HD, 3.5% H₂. 9-Bromobicyclo[5.3.0]dec-1(7)-ene (**6H**): ¹H NMR (250.1 MHz, CDCl₃) $\delta = 3.69$ (A₂B₂X system, $\delta_A = 2.77$, $\delta_B = 3.00$, $\delta_X = 4.49$, J(AB) = 15.0 Hz, J(AX) = 4.0 Hz, J(BX) = 7.0 Hz, 5 H), 2.11 (m, 4 H), 1.60 (m, 6 H); MS *m/z* (rel intensity) 214 (9, with isotope pattern), M⁺, 135 (58), 107 (37), 91 (100); HRMS calcd for C₁₀H₁₅⁷⁹Br 214.0310, found 214.0357.