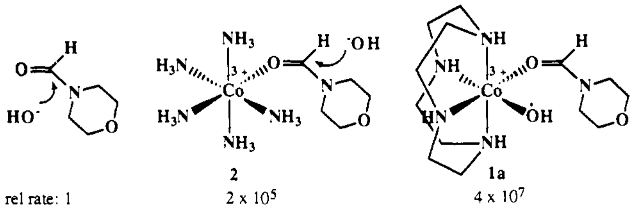
$[(cyclen)Co(OH)(OH_2)]^{2+}$ are 6 and 8, respectively).[8] Therefore, the metal-hydroxide in **1a** provides significant rate acceleration for the amide hydrolysis reaction.



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1a

Acknowledgment. Financial support was provided by the Natural Sciences and Engineering Research Council of Canada and the U.S. Army Research Office.

Rigid Bowlic Liquid Crystals Based on Tungsten-Oxo Calix[4]arenes: Host-Guest Effects and Head-to-Tail Organization

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Received September 15, 1992

New methodologies for the creation of noncentrosymmetric structures in molecular solids and liquids are critical to the development of new materials with ferroelectric and second order nonlinear optical (NLO) properties.[1,2] Liquid crystalline methods are particularly attractive since liquid crystalline materials are easily deposited for device construction and are readily aligned.[2] Bowl-shaped (bowlic) liquid crystals[3] are natural noncentrosymmetric building blocks since a head-to-tail organization maximizes the interactions between bowlic cores. Columnar phases are also conductive to polar order since their symmetry does not readily accommodate antiferroelectric arrangements.[3e] We present herein a new type of columnar liquid crystal with a rigid bowlic core based on tungsten-oxo calix[4]arene complexes. These complexes display mesophases of unusually high stability and novel host-guest effects, which suggests that head-to-tail organization occurs in the mesomorphic state.

Calix[4]arenes are a well-known class of bowlic compounds which have been of interest due to their ease of preparation and propensity to exhibit host-guest complexes.[5] We have synthesized azo-substituted calix[4]arene derivatives **2a** and **2b** as shown in Scheme I which have 8 and 12 side chains, respectively.[6] **2a** and **2b** are flexible macrocycles which, after recrystallization from solution, melt to give a transient mesophase which is only observed on first heating. Once heated into the isotropic phase, these compounds lose their mesomorphism and cooling produces only nonbirefringent glasses. Apparently, the crystal phase exhibits conformations compatible with a liquid crystal phase which are lost in the isotropic phase.[7]

Capping **2a** and **2b** with a tungsten-oxo group[4] to form **1a** and **1b** produces a mesogen with a rigid bowl conformation which promotes liquid crystallinity. Both **1a** and **1b** display columnar mesophases (M, M_1, and M_2) which are stable over a very wide temperature range as shown in Scheme II. The nature of the mesophases has been investigated by DSC, and optical textures were viewed with a polarizing microscope. The M to isotropic transition enthalpy for **1a** is fairly small (1.5 kcal/mol), indicating that this mesophase is likely a disordered phase with liquid-like correlation between mesogens. Cooling **1a**'s isotropic phase produces a texture for M characteristic of a columnar phase.[8] However, due to partial decomposition in the isotropic phase, we have not been able to generate textures by this method suitable for further analysis. **1b** displays two columnar phases M_1 and M_2, and the additional four side chains lower the clearing point to give a stable isotropic phase. The M_2-I transition enthalpy for **1b** is 5.1 kcal/mol, a value considerably greater than the isotropic transition enthalpy observed for **1a**. Miscibility studies determined that M and M_2 have different structures. By slow cooling of **1b**'s M_2 phase, a texture is produced with digitized contours, leaf patterns, and large regions of uniform extinction. The large areas of extinction are suggestive of a uniaxial structure, and the observation of digitized stars with 6-fold symmetry and 120° facets confirms a hexagonal arrangement of the columns in M_2.[9] The birefringence decreases with increasing temperature for both **1a** and **1b**, and there is a particularly large change between the mesophase and the crystal phase. This effect is likely the result of twisting motions of the azophenyls, which is also consistent with the observation that the mesophases of both complexes are yellow whereas the crystal phases are red. The large M_2-I transition enthalpy for **1b** and the spherulitic growth of the phase suggest that the mesogens are ordered in the columns, and therefore we characterize M_2 as a bowlic D_{ho} (these types of phases have also been termed P_A[3e,f] and B_{ho}[3g]). The small enthalpy of the M_1-M_2 phase transition and the absence of textural changes suggest that the structures of M_1 and M_2 are closely related.

The combination of the rigid cavity and the Lewis acidic nature of the square pyramidal tungsten produces a pronounced tendency for **1a** and **1b** to display host-guest interactions with Lewis bases.[4] Although a number of compounds may serve as guests, we have focused on DMF complexes due to their strong association, and 1:1 complexes are obtained by recrystallization from anhydrous DMF. Infrared spectroscopy confirms that DMF forms a Lewis base complex. The W=O band undergoes a characteristic shift from 1074 cm^{-1} (^{18}O 1019 cm^{-1}) to 990 cm^{-1} (^{18}O 938 cm^{-1}) with DMF complexation.[10] Likewise, the C=O band of the DMF

[†] Office of Naval Research Young Investigator 1992-1995, NSF Young Investigator 1992-1997.

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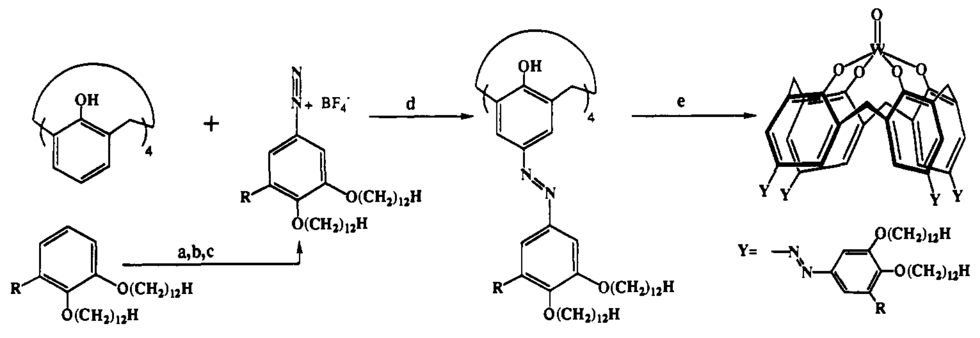
Scheme I



(a) SiO_2:HNO_3, (b) N_2H_4, graphite, (c) $NaNO_2$, HCl, $NaBF_4$ (d) Pyridine, (e) $WOCl_4$, Toluene

2a R=H
2b R=$O(CH_2)_{12}H$

1a R=H
1b R=$O(CH_2)_{12}H$

Scheme II

$$\mathbf{1a}\quad K \xleftrightarrow[19.8\ \text{kcal/mol}]{136°\text{C}} M \xleftrightarrow[1.5\ \text{kcal/mol}]{320°\text{C}} I_d$$

$$\mathbf{1b}\quad K \xleftrightarrow[7.9\ \text{kcal/mol}]{54°\text{C}} M_1 \xleftrightarrow[0.6\ \text{kcal/mol}]{77°\text{C}} M_2 \xleftrightarrow[5.1\ \text{kcal/mol}]{267°\text{C}} I$$

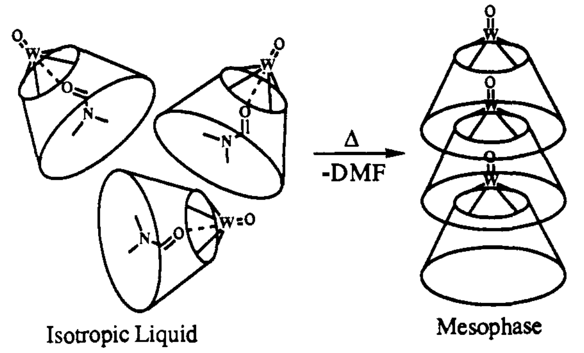
of the host–guest complex in CH_2Cl_2 solution occurs at 1645 cm^{-1}, which is 25 cm^{-1} lower in energy than uncomplexed DMF in CH_2Cl_2. The host–guest complexes exhibit more complicated ^1H NMR spectra with signals assigned to DMF at $\delta = 7.81$, 1.55, 1.36, and 0.58 ($CDCl_3$) and at $\delta = 8.05$, 0.41, 0.29, and 0.28 (C_6D_6).[11] The relative intensities of these signals were variable, depending on sample history; however, treatment of host–guest complexes with pyridine or diisopropylamine results in quantitative liberation of 1 equiv of DMF with signals at $\delta = 7.99$, 2.93, and 2.86 ($CDCl_3$). In addition, we found one of the calix[4]arene methylene resonances to be sensitive to the guests and shift from $\delta = 4.80$ to 4.85 ($CDCl_3$) with a DMF guest. The large upfield shift of the DMF protons is consistent with the shielding environment provided by the cavity.

The most dramatic consequence of host–guest complexation is its effect upon the mesomorphic behavior of the complexes. While **1a** exhibits a discotic mesophase from 135 to 330 °C, the DMF-**1a** host–guest complex melts directly to an isotropic phase at 115 °C (ΔH = 12.3 kcal/mol). Likewise, the **1b**–DMF host–guest complex melts to form an isotropic phase at 84 °C. Complexes with pyridine guests were found to exhibit isotropic transition at the same temperatures, indicating that a filled cavity is more important than the nature of the guest. With further heating (200–250 °C), the DMF slowly dissociates to form the discotic phase.

The depression of the isotropic phase through host–guest complexation allows the formation of a texture for **1a** consisting of well-defined cyclides with a tangential orientation of the optic axis characteristic of columnar phases.[8] Observation of these textures with a λ plate shows **1a** to exhibit unusual temperature dependent changes in the optic sign. These results are similar to those observed by others for bowlic liquid crystals.[3f] The K phase is optically positive; however, in heating cycles at temperatures just above K–M transition (<20 °C), the optic sign becomes negative. At higher temperatures the M phase becomes optically positive again. This transition to an optically negative material is not observed on cooling and is most likely due to conformational preferences of the azophenyl groups.

The deleterious effect of a DMF or pyridine guest on the mesophase stability indicates that occupation of the cavity is critical. This fact combined with the columnar structure of the mesophases suggests that the bowlic cores exhibit a head-to-tail arrangement whereby tungsten–oxo groups protrude into the cavity of the neighboring mesogen (Scheme III). The bowlic D_{ho} phase of **1b** is important since triangular symmetry dictates that the polar head-to-tail organization in the column must result in ferroelectric intercolumnar order or in a frustrated phase with random polarization. Additionally, the depression of the isotropic point through host–guest complexation provides a route to a low-viscosity state at reduced temperatures. This feature will allow for poling of very high melting bowlic complexes to produce noncentrosymmetric materials with high temporal stability.

Scheme III



Acknowledgment. We are grateful for financial support from the Office of Naval Research and to Dr. A. P. Sattelberger for a gift of $^{18}OH_2$.

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[11] Further investigations of host–guest complexation in these complexes is ongoing in our laboratory.

Synthesis, Crystal Structure, and Olefin Polymerization Activity of a Zwitterionic η^6-Arene Zirconium Tris(hydrocarbyl)

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Received July 28, 1992

The recent development of the chemistry of cationic dicyclopentadienyl group 4 metal–alkyl complexes,[1] $[Cp_2MR]^+$, functioning as single-component olefin polymerization catalysts has provided a key contribution to the understanding of the true active species involved in the metallocene-based Ziegler–Natta catalysts.[2]

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