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Novel Columnar Liquid Crystals Designed from Cone-shaped Calix[4]arenes. The Rigid Bowl Is Essential for the Formation of the Liquid Crystal Phase

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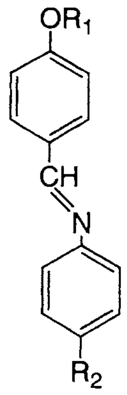
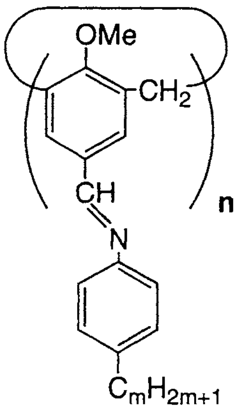
Conformationally-immobile calix[4]arenes with a cone conformation coupled to C_6H_4-*p*-C_mH_{2m+1} (m=3, 8, 12, 14, and 16) via an azomethine linkage were synthesized. It was found that the compounds with $m \geqq 8$ have the liquid crystal phase with a columnar arrangement.

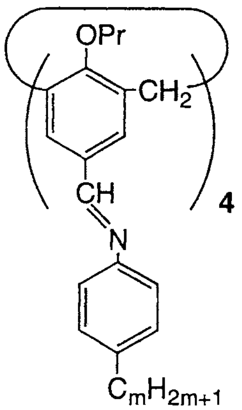
The search for thermotropic mesogenic materials is of great interest because of their physico-chemical properties and their potential applications. It is now known that liquid crystals are useful as novel media for stereoselective reactions,$^{1,2)}$ investigations of reaction mechanisms,$^{3,4)}$ control of ion-transport,$^{5)}$ etc.$^{6)}$ The essential idea that seems to be common among these investigations is related to unique characters of liquid crystals such as molecular orientation and phase transition. We considered that when liquid-crystalline compounds contain some molecule- or metal-binding site within a molecule, these characters are controlled by the subtle change induced by the guest-binding event. This idea stimulates molecular



Azomethine-type
liquid crystal



1_nC_m



2_4C_m

design of tubular or bowlic liquid crystals with a host molecule in the center surrounded by liquid-crystalline soft segments.[7,8] It occurred to us that calix[n]arenes, which serve as host molecules for metals and organic guests, may be useful as a central core for such columnar liquid crystals. With these objects in view, we previously synthesized a series of compounds $\mathbf{1}_n\mathrm{C}_m$ (n=4, 6, and 8; m=8, 12, 14, and 16) which include within the structure the basic skeleton of well-known azomethine-type liquid crystals.[9] We found that many of them show stable flow birefringence but only $\mathbf{1}_8\mathrm{C}_{16}$ gives the expected liquid crystal phase.[9] As reported elsewhere,[10] the calix[4]arene ring in $\mathbf{1}_4\mathrm{C}_m$ is quite flexible because the methoxy-through-the-annulus rotation is still allowed. We thus considered that the liquid crystal phase might appear when the rigid calix[4]arene is used as a central core. Since the propoxy group is bulky enough to inhibit the rotation,[10] we employed conformationally-immobile tetrapropoxycalix[4]arene with a cone conformation (as in $\mathbf{2}_4\mathrm{C}_m$). As expected, we have found that compounds $\mathbf{2}_4\mathrm{C}_m$ give the stable liquid crystal phase.

As reported previously,[9] $\mathbf{1}_4\mathrm{C}_m$ gave a single melting peak at 27-45 °C in the DSC measurement, which corresponds to a phase transition from amorphous to liquid phase. $\mathbf{2}_4\mathrm{C}_3$ gave a peak at 215 °C, which corresponds to a simple melting point. In contrast, $\mathbf{2}_4\mathrm{C}_m$ with $m \geqq 8$ gave rise to new peaks at around 30 °C (Fig. 1). It is seen from Fig. 1 that this phase transition consists of two peaks: with the increase in m, one at the low temperature region grows up to a large peak while another at the high temperature region remains as a sub-transition peak. The peaks at this temperature region are strongly affected by the chain length whereas those at the high temperature region are less affected and the ΔH values are almost constant (34.5-37.5 kJ mol^{-1}). The results support the view that the first phase transition is attributed to

Table 1. Phase transition properties of $\mathbf{2}_4\mathrm{C}_m$

m	Phase transition temperature (°C) and ΔH (kJ mol^{-1})			
	K ⟶ M		M ⟶ I	
	T	ΔH	T	ΔH
3			215[a)]	45.3[a)]
8	25	14.5	171	37.5
12	50	16.8	154	37.5
14	32	42.9	143	34.5
16	31	45.6	138	35.0

a) The values for K ⟶ I.

the "melting" of the aliphatic chains and the second phase transition is attributed to that of the azomethine-containing calix[4]arene bowl. This means that the liquid crystal phase appears owing to the balance between the association of the rigid cone-shaped core and the molecular motion of the flexible star-shaped aliphatic chains (Fig. 2).

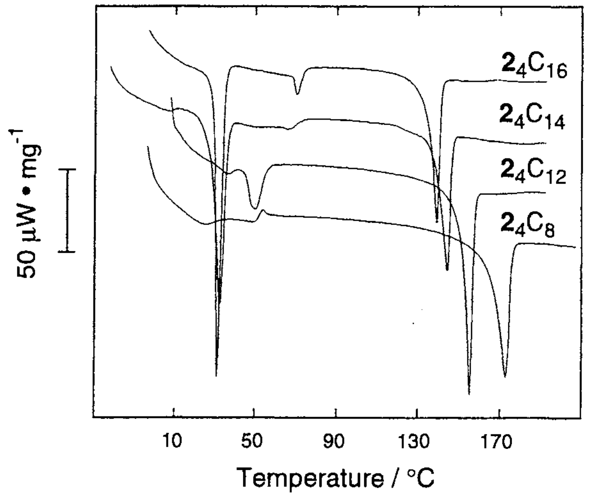


Fig. 1. DSC heating curves of 2_4C_m.

Fig. 3. Photograph of 2_4C_{16} at 50 °C under crossed Nicol prisms.

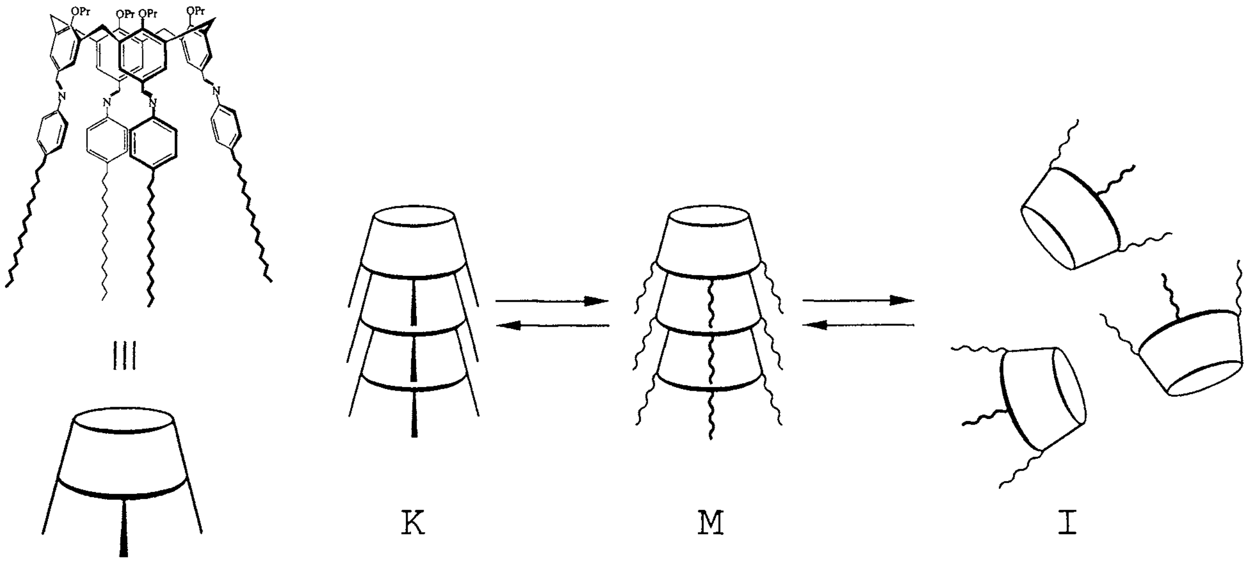


Fig. 2. Schematic representation of the phase transitions. In K the molecular motion of the aliphatic chains is frozen whereas in M it is allowed.

When **2_4C_{16}** was reduced by $NaBH_4$ to the $-CH_2-NH-$ derivative, the peak at the high temperature region disappeared while that at the low temperature region still remained (42 °C, ΔH= 84.3 kJ mol^{-1}). The finding also supports the phase transition mode illustrated in Fig. 2.

Under crossed Nicol prisms, the liquid crystal phase gave fan-like or angular textures (Fig. 3), which are known to be characteristic of a columnar mesophase. The preliminary X-ray diffraction study showed a long range orientation (2θ = 2.9°) and a short disordered orientation (2θ = 20°, broad). The CPK molecular model indicates that the diameter of **2_4C_{16}** including the aliphatic chains is about 30 Å. Thus, the long range orientation corresponds to the lattice constant arising from the columnar structure (2θ = 2.9° can be computed to 30 Å).

The present paper demonstrated that in star-burst-shaped calix[4]arenes, the amorphous phase is formed from a conformationally-mobile calix[4]arene core whereas the liquid crystal phase is formed from a conformationally-immobile calix[4]arene core. Very recently, Xu and Swager$^{11)}$ showed that the columnar mesophase is formed when the calix[4]arene conformation is immobilized through complexation with tungsten metal. Their finding is exactly complementary to our results. We are currently investigating if the host-guest-type interaction with the calix[4]arene induces the change in the phase transition properties.

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