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A New Class of Mesomorphic Materials Designed from Calix[n]arenes

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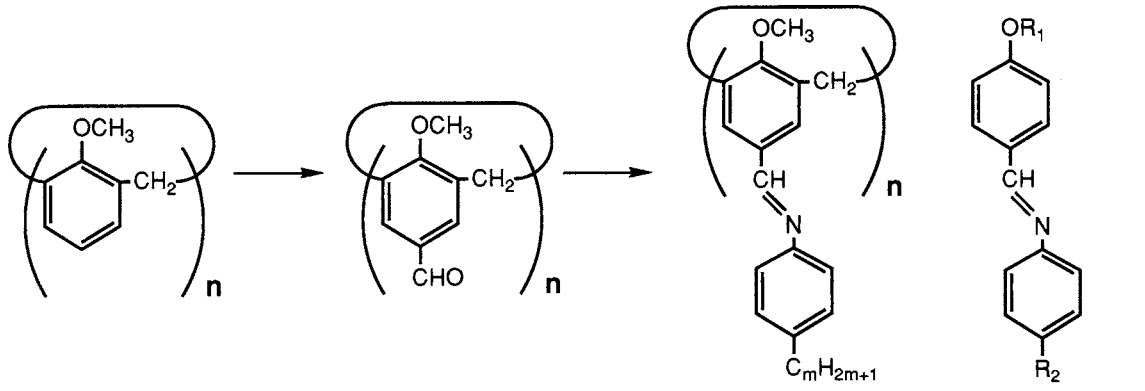
O-Methylated calix[n]arenes(n=4, 6, and 8) coupled to C_6H_4-p-C_mH_{2m+1}(m=8, 12, 14, and 16) via an azomethine linkage were synthesized. It was found that some of them show stable flow birefringence or readily form stable liquid crystals.

Calix[n]arenes having long aliphatic chains have been of increasing concern in host-guest chemistry and Langmuir monolayer formations.[1-3] We previously found that calix[n]arenes with p-dodecanoyl substituents aggregate through hydrogen-bonding interactions and act as novel gelators of organic fluids.[4] A series of these findings suggests that extension of calixarene-based host-guest chemistry to molecular assembly systems may provide a new chemistry field. We recently developed a new method to introduce the formyl group into the p-position of O-methylated calix[n]arenes($\mathbf{1}_n$).[5] From the compounds($\mathbf{2}_n$) one can easily synthesize the azomethine derivatives($\mathbf{3}_n\mathbf{C}_m$). Interestingly, compounds $\mathbf{3}_n\mathbf{C}_m$ include within the structure the basic skeleton of well-known azomethine-type liquid crystals. We thus carefully examined their aggregation properties and found out that they have amorphous or mesomorphic phases and show unique phase transition properties.



$\mathbf{1}_n$ $\mathbf{2}_n$ $\mathbf{3}_n\mathbf{C}_m$ azomethine-type liquid crystal

A mixture of 1_4(4.0 g, 8.3 mmol) and hexamethylenetetramine (42 g, 300 mmol) in trifluoroacetic acid (200 ml) was refluxed. The progress of the reaction was followed by HPLC. After 24 h, the mixture was poured into 500 ml of ice-water and extracted with chloroform. The chloroform solution was washed with water and dried over $MgSO_4$. Concentration of this solution followed by dilution with hexane gave the precipitate, which was recrystallized from chloroform-hexane: mp 216-218 °C, yield 76%. 2_6(mp >300 °C, yield 80%) and 2_8(mp 275-280 °C, yield 40%) were synthesized according to the similar method. A mixture of 2_4(148 mg, 0.25 mmol) and p-dodecylaniline (262 mg, 1.0 mmol) in 15 ml of chloroform was refluxed for 29 h in the presence of molecular sieves 4A 1/16. The work-up of the mixture gave 3_4C_{12} in a quantitative yield. Other 3_nC_m compounds were synthesized according to the similar method and identified by ^1H NMR, mass spectral evidence and elemental analysis.

3_4C_{14} and 3_4C_{16} were crystals and melted sharply at the temperatures recorded in Table 1. Thus, the phase transition for these compounds is mp (Tm) with the large ΔH value. In contrast, other calixarenes (except 3_8C_{16})

Table 1. Phase transition properties of 3_nC_m

3_nC_m		Tm or Tg[a]	ΔH	Properties[b]
n	m	°C	mJ mg^{-1}	
4	8	27	3.2	FB at 20-50 °C
4	12	20	2.7	FB at 10-40 °C
4	14	28	24.8	FB at 25-40 °C
4	16	45	44.0	FB at 35-50 °C
6	8	56	3.5	FB at 50-70 °C
6	12	42	2.2	FB at 35-50 °C
6	14	47	3.8	FB at 35-60 °C
6	16	40	8.4	FB at 30-50 °C
8	8	67	<1.0	FB at 60-80 °C
8	12	54	<1.0	FB at 45-65 °C
8	14	47	<1.0	FB at 40-55 °C
8	16	27, 49	8.5, 12	LC at 20-55 °C

a)Tm or Tg indicates peak temp in DSC.
b)FB=flow birefringence,LC=liquid crystal.

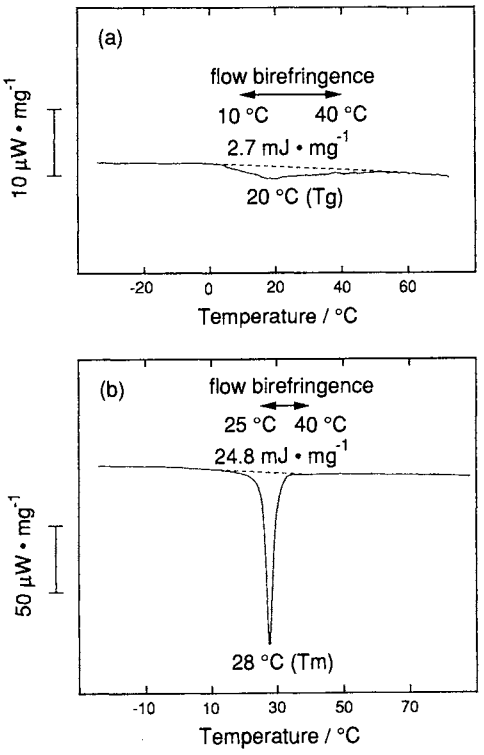


Fig. 1. DSC heating curves of (a) 3_4C_{12}, and (b) 3_4C_{14}.

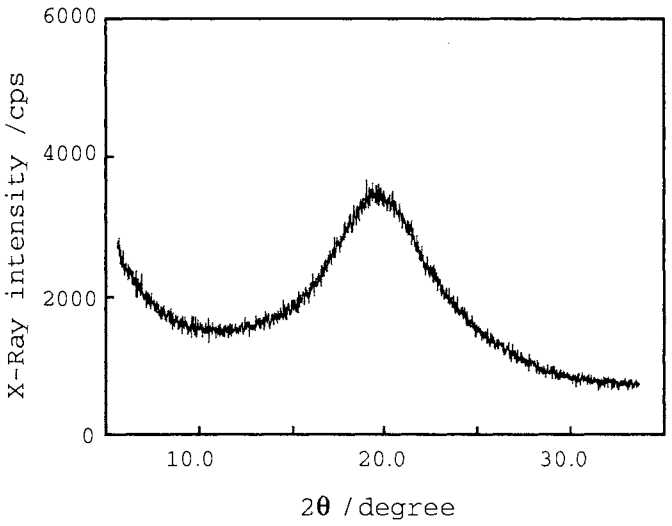


Fig. 2. X-Ray diffraction pattern of viscous compound 3_8C_{16} at 25 °C.

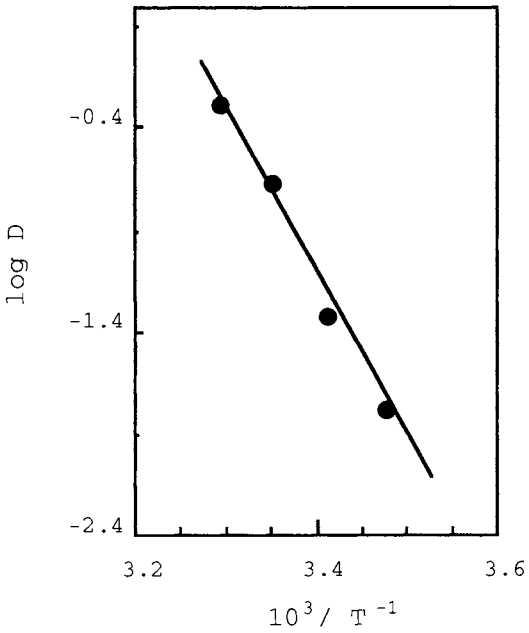


Fig. 5. Arrhenius plot for relaxation of FB in 3_4C_{12} : the relaxation rate was determined from the luminescence of 3_4C_{12} exhibiting birefringence under crossed Nicol prisms.

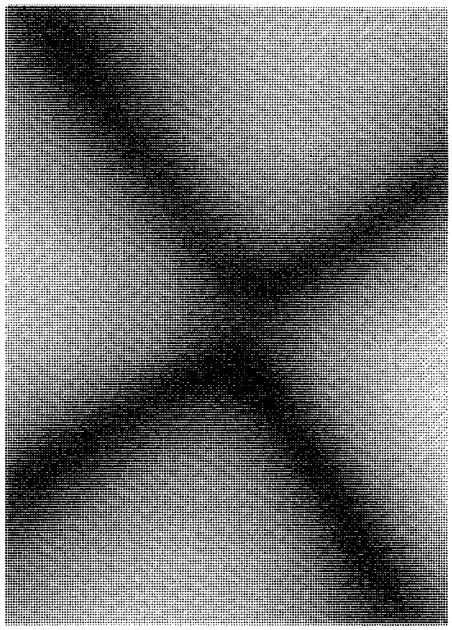


Fig. 3. Photograph of 3_4C_{12} turned concentric-circularly under crossed Nicol prisms.

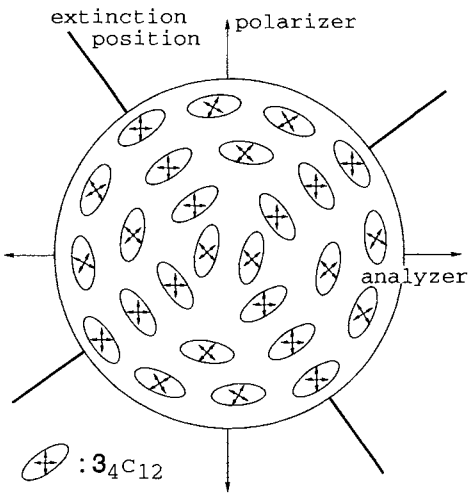


Fig. 4. Schematic presentation for concentric circular orientation of 3_4C_{12}.

were glassy solids and melted broadly. We consider that this phase transition with the small ΔH value is similar to the glass transition (Tg) observed for a polymer system. All compounds showed "flow birefringence(FB)" under crossed Nicol prisms. Of particular interest are compounds $\mathbf{3}_4C_{12}$ and $\mathbf{3}_8C_{16}$. $\mathbf{3}_8C_{16}$ gave two DSC endothermic peaks at 27 and 49 °C and behaved as a liquid crystal between 20 and 55 °C: this compound showed permanent birefringence under crossed Nicol prisms without external mechanical stress. The X-ray diffraction pattern of the viscous sample do not show any sharp peak characteristic of the crystal but a broad peak at $2\theta=19°$ (Fig. 2). This value (4.6 Å in distance) corresponds to the scattering of the aliphatic chains.

On the other hand, $\mathbf{3}_4C_{12}$ gave a broad endothermic DSC curve and a small ΔH value and showed stable FB at 10-40 °C. When two glass plates sandwiching viscous $\mathbf{3}_4C_{12}$ were slid under crossed Nicol prisms, the sample entirely shone. When two glass plates were turned concentric-circularly, a dark cross appeared in a white background (Fig. 3). This pattern implies that $\mathbf{3}_4C_{12}$ orientates in a concentric circular manner (Fig. 4). The bright patterns disappeared according to the first-order kinetics if the samples were left at room temperature. On the other hand, when they were left at 0 °C, the patterns were kept stably for several days. From the Arrhenius plot (Fig. 5) we estimated the activation energy for relaxation to be 38.0 kcal mol^{-1}.

In conclusion, the present paper suggests that amorphous and mesomorphic compounds derived from calix[n]arenes have several unique potentials for the development of new chemirecognics units, optical storage, and display devices.

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