

New Liquid Crystals with a Flexible Benzyloxytropone Core

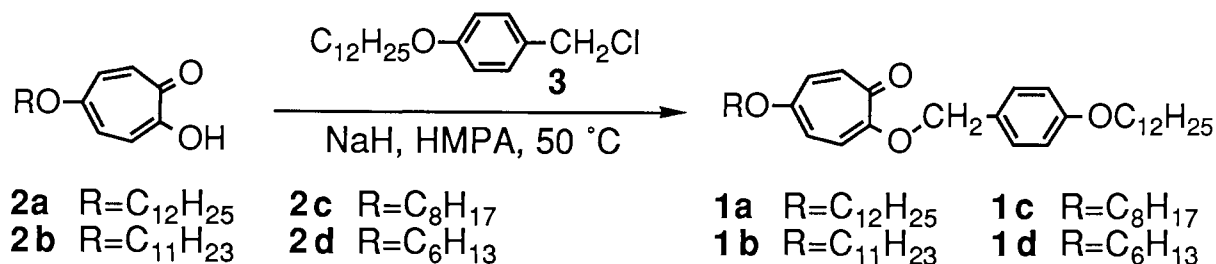
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2-Benzyloxytropones showed a monotropic smectic A phase while the corresponding alkoxybenzyl alkoxyphenyl ethers were nonmesogenic. The tropone carbonyl group acting as a dipolar lateral substituent enhanced the smectic thermal stability.

Recently, we prepared new liquid crystals with 2-acyloxy-5-alkoxytropone structures.^{1,2)} The benzoyl and alkanoyl groups can migrate (the [1,9] sigmatropy) between the two oxygen atoms at C-1 and C-2, whereas the 5-alkoxy-2-(4-methoxybenzyloxy)tropones and 2,5-dialkoxytropones do not show any [1,9] sigmatropy in solution and are nonmesogenic. Therefore, it is recognized that the [1,9] sigmatropy plays an important role to be mesogenic. It has been known that a wider molecular width and a flexible, saturated linking unit such as $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{CH}_2-$, and $-\text{OCH}_2\text{CH}_2\text{O}-$ are less favorable for an appearance of a mesophase.³⁾ However, when the alkyl groups at C-4 of the benzyloxy moiety were lengthened, the smectic A phase appeared. This paper describes the synthesis and mesomorphic properties of 2-benzyloxytropone derivatives.

5-Alkoxy-2-(4-alkoxybenzyloxy)tropones (**1a-d**) were prepared as follows: When the sodium salts of 5-alkoxytropolones (**2a-d**),¹⁾ prepared with NaH in HMPA at room temperature, were reacted with 4-dodecyloxybenzyl chloride (**3**) overnight at 50 °C, **1** were obtained in 42-65% yields after SiO_2 chromatography.⁴⁾ The ^1H NMR spectra of **1** showed no broadened signals at room temperature, eliminating an occurrence of [1,9] sigmatropy. The phase transition temperatures were determined by a differential scanning calorimeter (DSC) and the thermal behaviors of microscopic texture were



observed using a polarizing microscope equipped with a hot stage. The results are summarized in Table 1.

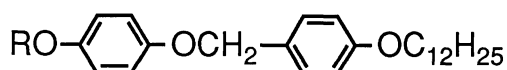
All mesogenic **1** showed a monotropic smectic A phase. This contrasts to that of corresponding benzenoids with a flexible, saturated linking unit, which are known to be nonmesogenic or mesogenic with low thermal persistence.³⁾ Actually, a benzene derivative (**4a**) did not exhibit any mesophase, whereas **4b** and **4c** showed a monotropic mesophase in a very short range.⁵⁾

Presumably the smectic phase can be stabilized by the tropone carbonyl group, whose permanent dipole moment increases the attractive dispersion force between molecules.⁶⁾ This is illustrated by non-sigmatropic and mesogenic 2-benzyloxy-tropone derivatives. The carbonyl group of tropones played a crucial role as a polar lateral substituent in the formation of the mesophase.

Table 1. Transition temperatures and enthalpy changes ^{a)}

R		Transition temp / °C (ΔH / kJ·mol ⁻¹)	
1 a	C ₁₂ H ₂₅	K $\xrightleftharpoons[55(42.3)]{83(44.7)} S_A \xrightleftharpoons[80(14.2)]{} I$	
1 b	C ₁₁ H ₂₃	K $\xrightleftharpoons[47(64.4)]{81(53.2)} S_A \xrightleftharpoons[77(13.7)]{} I$	
1 c	C ₈ H ₁₇	K $\xrightleftharpoons[52(50.0)]{81(50.1)} S_A \xrightleftharpoons[75(11.9)]{} I$	
1 d	C ₆ H ₁₃	K $\xrightleftharpoons[50(52.6)]{86(47.5)} S_A \xrightleftharpoons[70(9.0)]{} I$	

a) K: Crystals, I: Isotropic Liquid, S_A: Smectic A Phase.



4 a R=C₁₂H₂₅

4 b R=C₈H₁₇

4 c R=C₆H₁₃

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References

- 1) A. Mori, M. Uchida, and H. Takeshita, *Chem. Lett.*, **1989**, 591.
- 2) A. Mori, H. Takeshita, K. Kida, and M. Uchida, *J. Am. Chem. Soc.*, **112**, 8635 (1990).
- 3) G. W. Gray, "The Molecular Physics of Liquid Crystals," ed by G. R. Luckhurst and G. W. Gray, Academic Press (1979), Chap. 1.
- 4) The compounds described in this paper showed pertinent figures of elemental analyses and spectral data.
- 5) The microscopic texture was similar to that of the typical smectic B phase. Detailed studies are in due course.
- 6) K. Takatoh, K. Sunohara, and M. Sakamoto, *Mol. Cryst. Liq. Cryst.*, **164**, 167 (1988).

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