CHEMISTRY LETTERS, pp. 931-932, 1994.

A New Family of Liquid Crystals with Low Melting Points. 4-(*trans*-4-Alkylcyclohexyl)-alkylbenzenes

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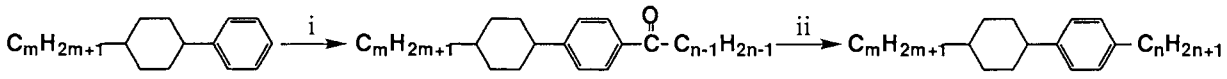
Four homologues of 4-(*trans*-4-alkylcyclohexyl)-alkylbenzene were prepared and their liquid crystal properties were investigated. These homologues comprise an interesting and useful family of nematic liquid crystals with melting points below 0 °C. Eutectic mixture of these four compounds gave a stable nematic phase at temperatures between -22.8 and -50.2 °C.

We recently proposed a polymerization method for obtaining an aligned polyacetylene film by using a liquid crystal as a polymerization solvent,[1-4] and we found that some homologues of 4-(*trans*-4-alkylcyclohexyl)-alkylbenzene could be useful components of liquid crystal solvent for controlling the polymerization temperature.[3] Although the basic chemical structure of these homologues have been developed by Eidenschink,[5] their mesomorphic properties have not been fully investigated because one of these homologues has no observable nematic phase. We, therefore, selected four homologues of 4-(*trans*-4-alkylcyclohexyl)-alkylbenzene and investigated their liquid crystal properties. Because the alkyl chain length of a terminal group is critical for forming a mesomorphic phase (which is well known as an odd-even effect), we chose propyl and pentyl terminal groups. As a result, we found that these homologues comprise an interesting and useful family of nematic liquid crystals. They all have melting points below 0 °C and one of these compounds is an enantiotropic nematic liquid crystal.

4-(*trans*-4-Alkylcyclohexyl)-alkylbenzenes (**3**) were prepared with methods similar to those proposed by Szczucinski et al.[6](Scheme 1). Friedel-Crafts acylation of **1** (which were commercially available) with acid chloride (1.3 equiv.) and $AlCl_3$ (1.7 equiv.) in methylene chloride at 0 °C afforded the ketones (**2**). Wolff-Kishner reduction of **2** by hydrazine hydrate (5.3 equiv.) in the presence of the base in diethylene glycol at 200 °C gave the desired compounds (**3**). The products **2** and **3** were identified by elemental and spectral analyses, including IR and NMR spectra.



1a-d **2a-d** **3a-d**

1a-d	**2a-d**	**3a-d**
a: m=3	**a**: m=3, n=3	**a**: m=3, n=3
b: m=3	**b**: m=3, n=5	**b**: m=3, n=5
c: m=5	**c**: m=5, n=3	**c**: m=5, n=3
d: m=5	**d**: m=5, n=5	**d**: m=5, n=5

Scheme 1. Reagents and conditions : i) $C_{n-1}H_{2n-1}COCl$, $AlCl_3$, in CH_2Cl_2, 0 °C, 3 h, ii) $H_2NNH_2{\cdot}H_2O$, KOH in diethylene glycol, reflux, 2 h.

Table 1. Mesomorphic transition temperatures and latent heats of melting for the 4-(*trans*-4-alkylcyclohexyl)-alkylbenzenes

Compounds	m	n	Transition temperatures / °C C-N, or I	S-N	N-I	Latent heats kcal / mol
3a	3	3	-13.4		[-48.0]	4.6
3b	3	5	-8.7		[-30.0]	4.6
3c	5	3	-10.2		(-13.0)	4.4
3d	5	5	-4.5	(-8.1)	-4.2	4.7

C = Crystal; S = Smectic; N = Nematic; I = Isotropic liquid. Parentheses denote a monotropic phase transition and square brackets a virtual phase transition.

Mesomorphic transition temperatures and latent heats of melting for the four compounds are listed in Table 1. The calorimetric curves were recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter during heating and cooling. The heating rate in this work was 5 °C / min. The temperatures were calibrated with the transition point and melting point of cyclohexane (-87.1 °C and 6.6 °C). The heat capacity was calibrated with the latent heat of melting of indium (13.8 kcal / mol). The observed mesophases were identified by using a polarizing microscope to examine the texture. The compounds **3a** and **3b** are virtual liquid crystals and their virtual N-I transition temperatures were estimated by the extrapolation of the transition curves obtained in the binary systems with the compound **3c**. The compound **3c** is a monotropic mesogen and the compound **3d** is an enantiotropic one. In the case of **3d**, a smectic phase was also observed. The compound **3d** is, to the best of our knowledge, the first enantiotropic nematic liquid crystal to have a melting point below 0 °C. It is worth noting that all four of these compounds have melting points below 0 °C. So far, a low melting temperature for a liquid crystal has often meant room temperature.[7] Therefore, the 4-(*trans*-4-alkylcyclohexyl)-alkylbenzenes reported here are just classified as a family of low melting-point liquid crystals.

Because of the low melting points, eutectic mixture of these four compounds gave a stable nematic phase at temperatures between -22.8 and -50.2 °C. The eutectic composition was calculated from the melting points and latent heats of melting.[8] This eutectic mixture is a liquid crystal solvent suitable for low temperature polymerization of polyacetylene, and such an experiment is in progress. We also found that the ketones (**2a-d**) were mesomorphic compounds. Their liquid crystal properties will be reported elsewhere.

We would like to thank Dr. T. Kitamura for many useful discussions on liquid crystals and Japan High Tech Co. for microscopic observations.

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(Received February 22, 1994)