CHEMISTRY LETTERS, pp. 79 - 82, 1985.

NEW LIQUID CRYSTALLINE COMPOUNDS. 2-(p-CYANOPHENYL)-5-ALKYL-1,3-OXATHIANES

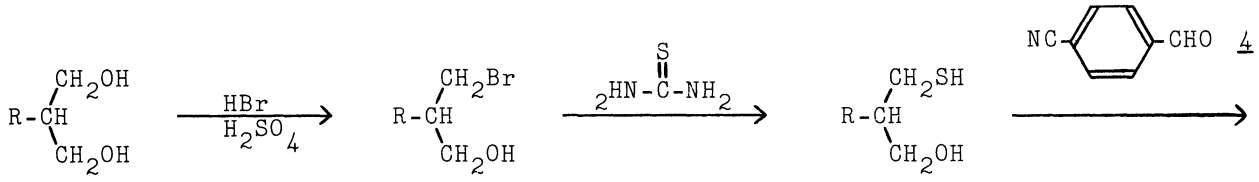
Yuichiro HARAMOTO * and Hiroyoshi KAMOGAWA

Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400

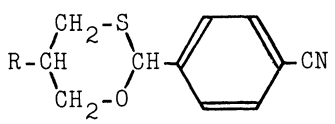
2-(p-Cyanophenyl)-5-alkyl-1,3-oxathianes having the monotropic nematic liquid-crystal phase around room temperature were synthesized and their liquid-crystal behavior was compared with those of the corresponding 1,3-dithianes and 1,3-dioxanes.

In recent years, 2,5-disubstituted-1,3-dithianes and several 2,5-disubstituted-1,3-oxathianes have been reported as a new types of liquid-crystalline compounds.[1-3] While 2-(p-cyanophenyl)-5-alkyl-1,3-dithianes synthesized in a previous work did not exhibit any liquid-crystal phases, 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes synthesized this time have exhibited the monotropic nematic liquid-crystal phase at room temperature. In this communication, we wish to present the mesomorphic behavior of 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes in comparison with those of the corresponding 1,3-dithianes and 1,3-dioxanes.

2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes were synthesized via the following route



1 2 3



5

R: n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}

In step 1 - 2, the reaction temperature must be kept between 70 and 75 °C.

At a temperature between 90 and 95 °C, the main product was the disubstituted bromide contrary to purpose. As compounds 3 was susceptible to oxidation, step 2 → 3 must be done under a nitrogen atmosphere. In 3 → 5, both trans and cis isomers differing at the C-5 position of the 1,3-oxathiane ring were produced. Several time recrystallizations were required to effect separation of trans from cis isomers. As trans and cis isomers exhibit C2 proton signals of the 1,3-oxathiane ring in ^{1}H-NMR at δ=5.75 and 5.80, respectively, the presence of cis isomer can be detected by the examination of proton signals at δ=5.80. The presence of 1,3-dithianes can also be detected by the examination of C2 proton signals at δ=5.10. Absorptions of C2, C4, and C6 carbons of the 1,3-oxathiane ring in ^{13}C-NMR spectra, as determined by ^{1}H-complete decoupling (COM), ^{1}H-off resonance decoupling (OFR), and ^{1}H-selective decoupling (SEL) procedures, are located at δ=83.22, 34.84, and 75.53, respectively (R=C_8H_{17}).

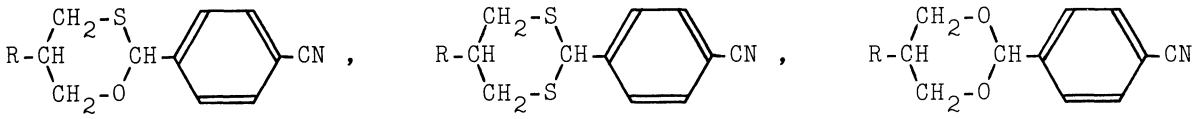
Measurements of mesomorphic ranges and assignment of the mesophases were carried out by means of a micro melting-point apparatus equipped with polarizers. Mesomorphic ranges of the synthesized 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes and the corresponding 1,3-dithianes and 1,3-dioxanes are given in Table 1. Compounds 5 and 6 were purified until only a single spot in t.l.c. (ether-hexane).

Transition temperatures of isotropic to nematic (Tn-i) for 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes were lower than those for the corresponding 1,3-dioxanes by about 20 °C. (Table 1) It is known generally that, the larger the molecular width, the lower is Tn-i.[4] The width of 2-(p-cyanophenyl)-5-alkyl-1,3-oxathianes is larger than that of the corresponding 1,3-dioxanes because of the presence of a large sulfur atom. While compounds 5 exhibit the monotropic nematic liquid-crystal phase, compounds 6 did not exhibit any liquid-crystal phases. Since molecular width increases in the order: 1,3-dioxane, 1,3-oxathiane, 1,3-dithiane, 1,3-dithianes with larger molecular widths appear to cause smaller molecular interactions, so that any liquid crystal phases might not be exhibited.[5] In compounds 5 with a short alkyl chain (R=C_3H_7, R=C_4H_9), any liquid-crystal phases are not observed. Accordingly, the length of R affects the appearance of liquid-crystal phases. In compounds 5 having an alkyl chain with odd carbon number tend to have somewhat higher values of Tn-i (R=C_5H_{11}, 19 °C; R=C_7H_{15}, 30 °C), whereas those having an alkyl chain of even carbon number tend to have somewhat lower values (R=C_6H_{13}, 17 °C; R=C_8H_{17}, 26 °C). In compounds 5, the differences between transition temperatures of crystal to isotropic (Tc-i) and

those of isotropic to nematic (Tn-i) are very large. (for example, R=C_5H_{11}, Tc-i − Tn-i = 55 °C). This property seems to be its own. ⊿Hc-i of the compounds 5-3, 5-4, 5-5, and 5-6 are 5.42 Kcal/mol, 5.97 Kcal/mol, 7.26 Kcal/mol, and 6.25 Kcal/mol (1cal=4.184J) respectively. These values are as same as those of other common liquid-crystal materials.[6)]

The principal features of the mesomorphic behavior of compounds 5 are (1) to exhibit the monotropic nematic liquid crystal phase around ordinary room temperature, and (2) to have large differences between Tc-i and Tn-i.

Table 1. Mesomorphic ranges for compounds 5, 6, and 7



5 6 7

	R	Mesomorphic range / °C[a)]		R	Mesomorphic range / °C[a)]
5 - 1	n-C_3H_7	C 97 → ← 21 I	6 - 4	n-C_6H_{13}	C 90 → ← 36 I
5 - 2	n-C_4H_9	C 94 → ← 15 I	6 - 5	n-C_7H_{15}	C 98 → ← 43 I
5 - 3	n-C_5H_{11}	C 74 → I, I ⇄ N 19, N ⇄ 11 C	6 - 6	n-C_8H_{17}	C 93 → ← 39 I
5 - 4	n-C_6H_{13}	C 73 → I, I ⇄ N 17, N ⇄ 6 C	7 - 1	n-C_4H_9	C 42 → I, I ⇄ N 35.5, N ⇄ C c)
5 - 5	n-C_7H_{15}	C 78 → I, I ⇄ N 30, N ⇄ 15 C	7 - 2	n-C_5H_{11}	C 55 → I, I ⇄ N 48, N ⇄ C
5 - 6	n-C_8H_{17}	C 70 → I, I ⇄ N 26, N ⇄ 15 C	7 - 3	n-C_6H_{13}	C 47 → I, I ⇄ N 40.5, N ⇄ C
6 - 1	n-C_3H_7	C 133 → ← 78 I b)	7 - 4	n-C_7H_{15}	C 54 → I, I ⇄ N 52, N ⇄ C
6 - 2	n-C_4H_9	C 88 → ← 30 I	7 - 5	n-C_8H_{17}	C 60 → I, I ⇄ N 51, N ⇄ C
6 - 3	n-C_5H_{11}	C 98 → ← 28 I			

a) C=crystal; N=nematic; I=isotropic. b) Cited from Ref. 2.

c) Cited from Ref. 7.

References

1) Y. Haramoto and H. Kamogawa, J. Chem. Soc., Chem. Commun., 1983, 75.

2) Y. Haramoto, A. Nobe, and H. Kamogawa, Bull. Chem. Soc. Jpn., 57, 1966 (1984).

3) Y. Haramoto, K. Akazawa, and H. Kamogawa, Bull. Chem. Soc. Jpn., 57, 3173, (1984).

4) G.W. Gray and B.W. Worrall, J. Chem. Soc., 1545, (1959).

5) G.W. Gray and B. Jones, Nature, 170, 451, (1952).

6) G.W. Gray and P.A. Winsor, "Liquid Crystals & Plastic Crystals," Wiley, New York, (1974), Vol. 2, p.254.

7) D. Demus and H. Zaschke (to V.E.W. Kombinat Mikroelectronik), Japan Pat. Appl. No 54-160916, Dec. (1979).

(Received October 23, 1984)