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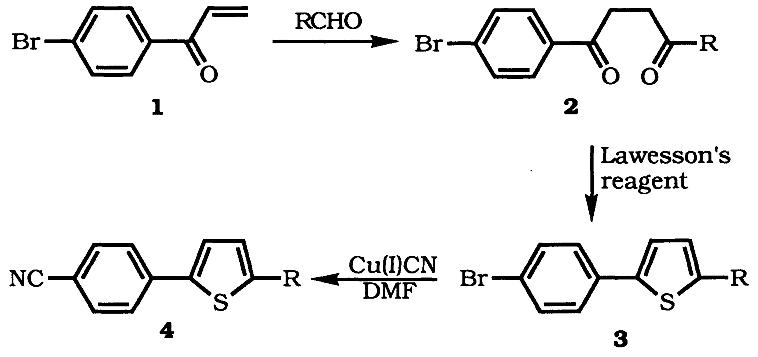
New Liquid Crystalline Compounds Based on Thiophene

Roger BRETTLE, David A. DUNMUR, Charles M. MARSON,
Milagros PIÑOL, and Kazuhisa TORIYAMA
Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK,

A homologous series of 2-alkyl-5-(4'-cyanophenyl)thiophenes has been prepared and shown to have improved properties for use in liquid crystal displays. The thiophene ring is prepared from a 1-(4'-bromophenyl)-1,4-dioxoalkane, constructed using the Stetter procedure, by the action of Lawesson's reagent, and the cyano-group is finally introduced using a copper(I)-mediated exchange reaction.

Many liquid crystal molecules have a benzene ring as an essential part of their rigid core.1) Use of a thiophene ring which has comparable aromaticity in place of a benzene ring introduces a non-linear element into the structure, and might be expected to yield compounds with mesophases at lower temperatures. Some liquid crystal compounds containing a thiophene ring have been prepared, but these either exhibit only a smectic phase or high temperature nematic phases. Furthermore they often incorporate linking groups within the molecule which make them chemically unstable.2) It was thought that if a cyano-group was present in compounds based on a thiophene core, chemically stable materials exhibiting a low temperature nematic liquid phase would result. The value of low melting mesophases is that they can be used in mixtures to reduce viscosity, and hence decrease switching times in display applications.

In the present work we report the synthesis of a series of compounds of the type **4**. The Mannich reaction on 4-bromoacetophenone,3) followed by quaternisation and elimination under mildly basic conditions4) gave the α,β-olefinic ketone **1** in 71% yield. This, when condensed with an alkanal in the presence of a thiazolium catalyst, using the Stetter procedure,5) gave the 1,4-diketone in 76-87% yield. Treatment of the 1,4-diketone with Lawesson's reagent then gave the thiophene **3** in 58-71% yield.6) Finally, exchange of the bromo-subtituent for a cyano-group was accomplished in 79-88% yield with copper(I) cyanide in boiling DMF.7)



$R = C_nH_{2n+1}$, n = 3-11

All compounds **4** were colourless, showing good stability on storage under normal conditions. They had low melting points, and monotropic mesophase behaviour was observed with n = 3,4,5,6 and 8. Nematic phases were observed as expected due to the presence of the nitrile group, and the octyl homologue also exhibited a S_A phase on cooling from the monotropic nematic phase. For the non-mesogenic members of the series $(T_{NI})_{virtual}$ were extrapolated from measurements on mixtures containing approximately a 20% molar ratio of the thiophene derivative using 4-pentyl-4'-cyanobiphenyl as the nematic solvent. Transition temperatures and phase behaviour are represented schematically in Fig. 1, and full mesophase data is given in Table1.

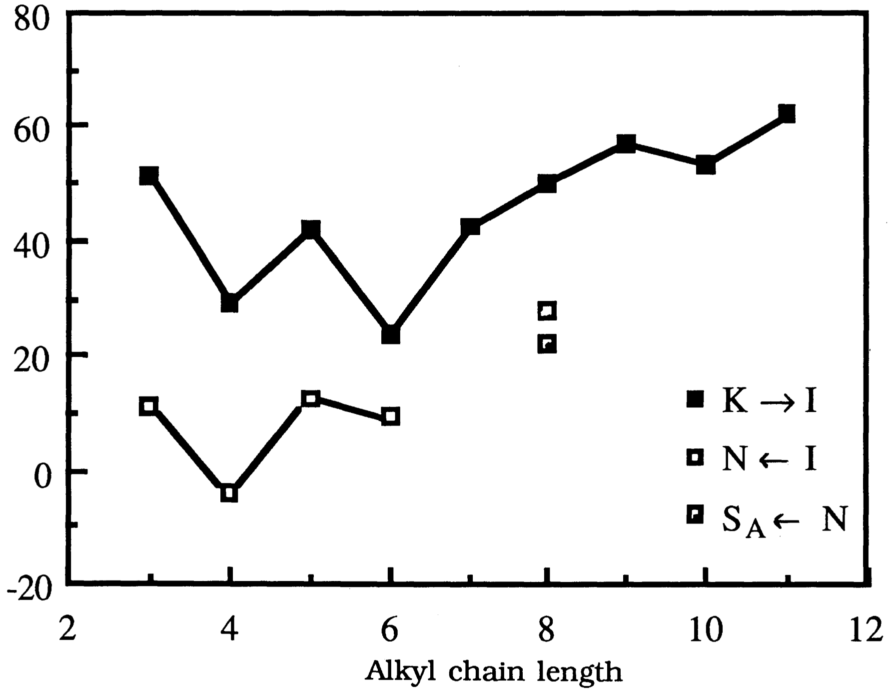


Fig.1. Transition temperatures as a function of chain length for alkyl-cyanophenyl thiophenes.

Table 1. Thermal data for 2-alkyl-5-(4-cyanophenyl)thiophenes **(4)**

n	Transition	T_{OPT}/°C a)	T_{DSC}/°C a)	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
3	K→K'	44.0b)	36.4	14.20d)	--
	K→I	44.7b)	--	--	--
	K'→I	51.4	49.2	80.14d)	--
	(I→N)c)	11.3	e)	--	--
4	K→I	29.2	28.0	17.95	59.61
	(I→N)c)	-3.9	f)	--	--
5	K→I	42.0	39.2	27.72	88.75
	(I→N)c)	12.3	8.8	-0.26	-0.92
6	K→K'	2.5	-3.8	2.55	9.46
	K'→K"	8.6	9.2	g)	g)
	K"→K"'	13.5	15.0	12.37h)	--
	K"→I	18.9	18.0	64.71h)	--
	K"'→I	24.0	23.0	3.71h)	--
	(I→N)c)	9.5	5.8	-0.54	-1.92
7	K→I	42.2	43.0	33.02	104.45
	N→Ii)	22.2	--	--	--
8	K→I	49.9	46.9	36.23	113.21
	(I→N)c)	22.2	j)	--	--
	(N→S_A)c)	20.8	j)	--	--
9	K→I	57.2	55.4	43.18	131.44
	N→Ii)	29.7	--	--	--
10	K→I	53.4	51.6	43.56	134.12
	N→Ii)	19.7	--	--	--
11	K→K'	50.0	48.6	39.18	117.18
	K→I	56.0	k)	--	--
	K'→I	62.0	61.3	11.33	35.22
	N→Ii)	40.5	--	--	--

a)T_{OPT} is transition temperature observed under the microscope and T_{DSC} the onset temperature calculated from DSC plot. b) Complex peak probably including K→K' and K→I. c) Monotropic transition. d) Values given in J g^{-1}; sample size 1.29 mg. e) Complex crystallization peak between 24 and 37 °C. f) Complex crystallization peak between 2 and -22 °C. g) 2nd Order transition, ΔCp = 1.146 J g^{-1} $°C^{-1}$. h) Values given in J g^{-1}; sample size 1.70 mg; two crystal forms present. i) Virtual T_{NI}. j) Complex crystallization peak between 19 and 40 °C. k) Not observable on DSC.

For some of the homologues (n = 3, 6, and 11) two melting points were observed depending on the heating rate. We postulate the existence of two crystal forms with different melting points and suggest the following sequence for the heating/cooling process as illustrated for the propyl homologue. Particular homologues with n = 5 and 7 were examined as components of mixtures suitable for TN display devices.[8)] It was found that these mixtures were of low viscosity (≈30cP) and high dielectric anisotropy (≈11) at room temperature, thereby demonstrating the usefulness of the thiophene derivatives described above for liquid crystal applications.

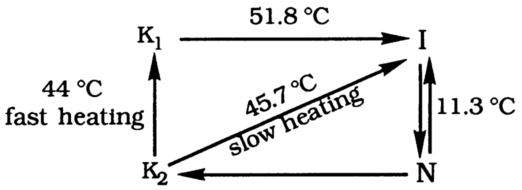


Fig. 2. Proposed behaviour for the propyl homologue of the thiophene series.

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