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The Preparation of 4-Cyano-4′-Alkyltolans

A New Series of Liquid Crystals

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The preparation of a new series of liquid crystal compounds, the 4-cyano-4′-alkyltolans, starting from the corresponding stilbenes, is described. A preliminary determination of the transition temperatures by polarized light microscopy is also included in this paper.

Tolans substituted in the 4- and 4′- positions either with alkyl and alkoxy groups, or with alkoxy groups in both positions have been prepared and their liquid crystalline properties studied by Malthete and co-workers. We subsequently prepared a series of 4-alkyl-4′-cyanostilbenes[2] and are currently studying their thermodynamic properties. In order to compare the effect of changing a *trans*-double bond to a triple bond in compounds with the 4-alkyl-4′-cyano substitution pattern and with the single bonded structures prepared by Gray,[3] we have now synthesized a series of 4-alkyl-4′-cyanotolans. This paper describes the preparation of these compounds and reports the preliminary results of investigations of their liquid crystal properties.

Tolans can be prepared by several standard synthetic procedures, most of which lead to symmetrically substituted compounds. The method that Malthete and co-workers[1] used for the preparation of unsymmetrically substituted tolans, involving the alkaline rearrangement of 1,1-di-substituted ethylenes, could not be used in our case because the Grignard reaction used in this method could not be carried out in the presence of the cyano group. We therefore decided on a synthesis starting from the corresponding stilbenes which we had previously prepared.[2] These compounds which were always obtained as a mixture of *cis*/*trans* isomers were brominated to the dibromide with pyridinium bromide perbromide in acetic acid.

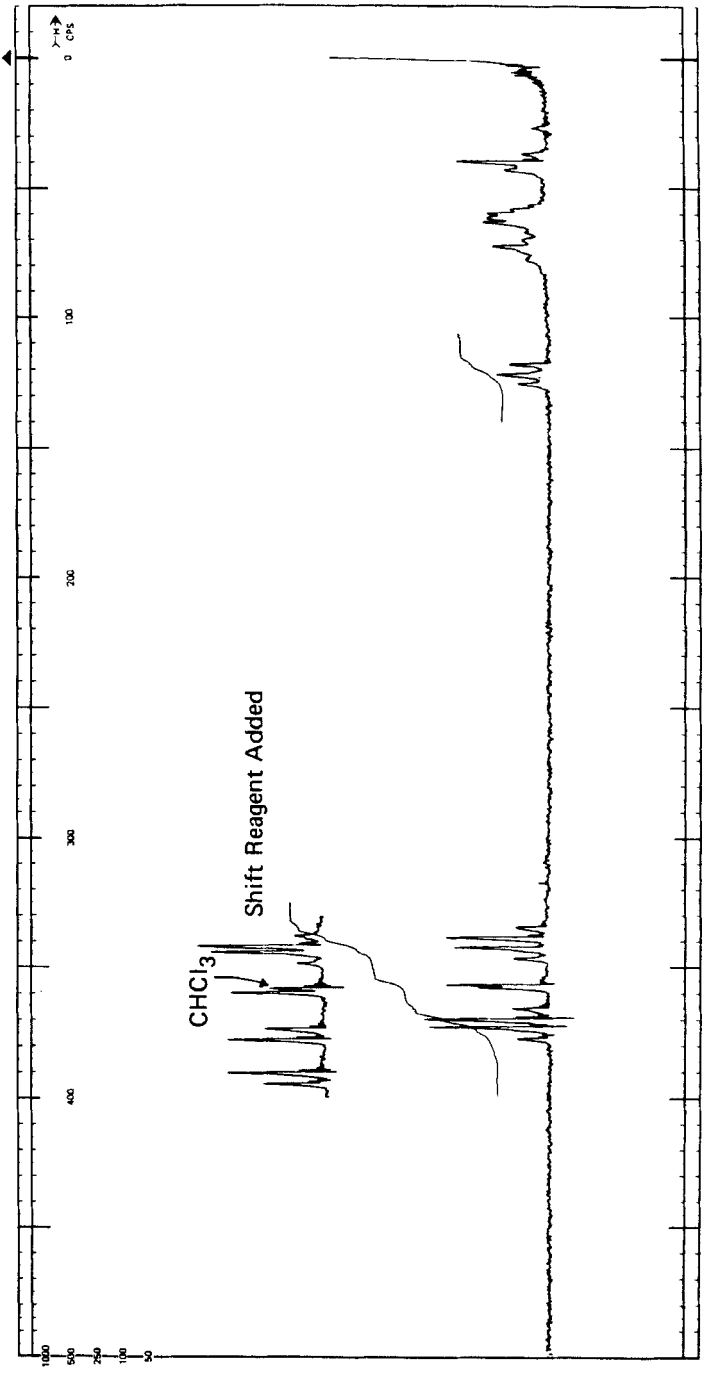


FIGURE 1 N.M.R. spectrum of 4[1(or 2) bromoethenyl-2(or 1)-(4′-*n*-pentyl)phenyl)] benzonitride.

Dehydrobromination could be carried out by heating with a strong base. This invariably hydrolyzed the cyano group and it was found necessary to use 1,5-diaza-bicyclo[5,4,0]undec-5-ene (D.B.U.) as the base. The cyano group remained completely intact using this reagent. However, the reaction required refluxing in dimethyl formamide in order to remove both bromine atoms and give the tolan. Heating on a steam bath for as long as two hours resulted in removal of only one bromine and produced an α-bromostilbene. It has not been established which of the two isomeric α-bromostilbenes was prepared although the NMR spectrum shown in Figure 1 indicated only a single compound. It would seem probable that the more acid proton on the carbon adjacent to the ring substituted with the cyano group would be lost most readily by reaction with D.B.U., thus leaving the bromine substituted on that position. C^{13}NMR shown in Figure 2 supported the contention of a single isomer but failed to locate the bromine substituted carbon. Microscopy failed to detect any sign of liquid crystallinity in these materials. This is rather surprising in view of the nematogenic behavior of the α-chloro-stilbenes,[4] on the other hand it is possible that the larger bromine atom simply depresses the liquid crystal phase too far to allow it to be detected.

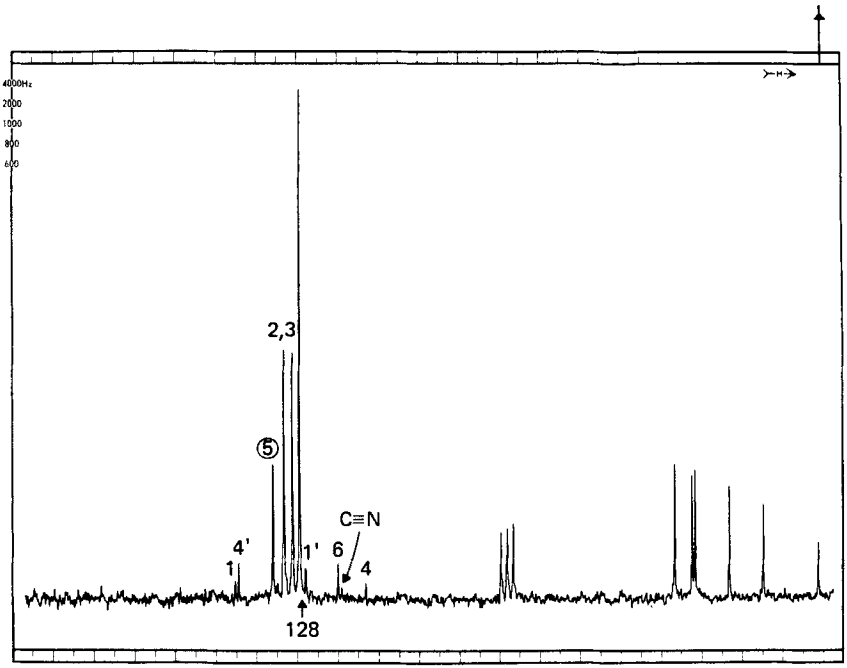


FIGURE 2 C^{13}N.M.R. spectrum of 4[1(or 2) bromoethenyl-2(or 1)-4'-*n*-pentylphenyl)] benzonitride.

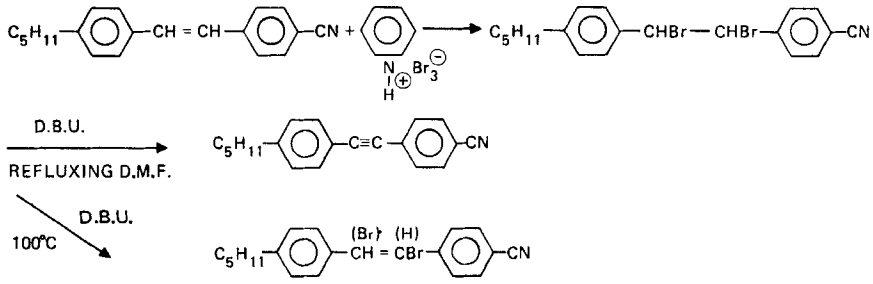
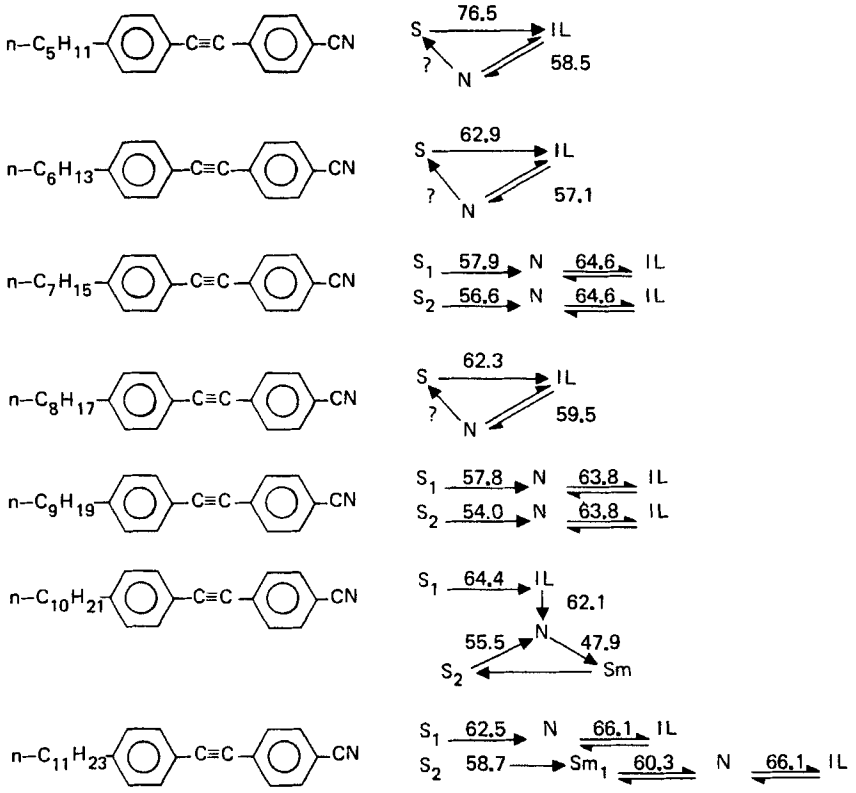


FIGURE 3 Reaction sequence for the preparation of 4-cyano-4′-alkyltolans.



S = Crystal (solid)
N = Nematic
Sm = Smectic
IL = Isotropic Liquid

FIGURE 4 Melting and liquid crystal transition temperatures of 4-cyano-4′-alkyltolans.

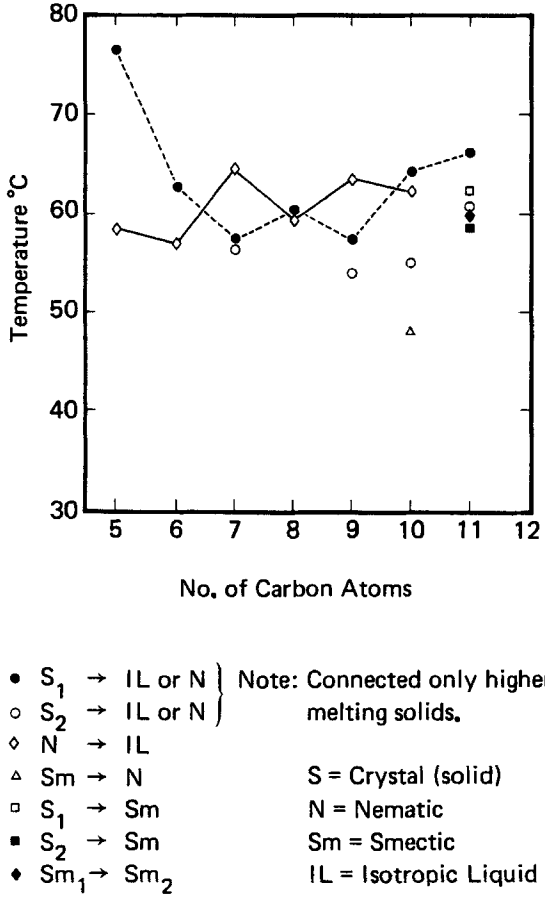


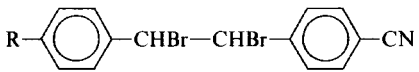
FIGURE 5 Plot of carbon atoms in paraffinic tail against transition temperature for 4-cyano-4'-alkyltolans.

The reaction sequence used in the preparation of these compounds is shown in Figure 3. Figure 4 shows the mesophases and transition temperatures obtained by optical microscopy.

A plot of the numbers of carbon atoms in the paraffinic tail against the transition temperatures shown in Figure 5 exhibits the usual odd-even alternation found in such series of liquid crystals. Tables I and II list the physical properties and yields obtained for the new intermediates and liquid crystals.

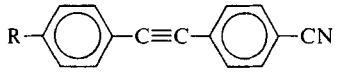
Detailed studies of the thermal properties of these compounds are currently in progress and will be reported shortly.

TABLE I



R	% Yield	M.P. °C	Recrystallization solvent	Elemental analysis							
				Calculated				Found			
				C	H	N	Br	C	H	N	Br
n-C_5H_{11}	57	161–2	Ethanol	55.2	4.9	3.2	36.7	55.1	4.8	3.2	36.3
n-C_6H_{13}	31	149–50	Ethanol	56.1	5.2	3.1	35.6	56.1	5.1	3.0	36.1
n-C_7H_{15}	38	145–6	Ethanol	57.0	5.4	3.0	34.5	51.0	5.5	3.0	34.6
n-C_8H_{17}	36	145–6	Ethanol	57.9	5.7	2.9	33.5	57.7	5.8	2.9	33.9
n-C_9H_{19}	62	144–5	Ethanol	58.7	5.9	2.8	32.5	58.8	5.9	2.9	32.8
n-$C_{10}H_{21}$	46	141–2	Ethanol	59.4	6.2	2.8	31.6	58.7	5.9	2.9	31.8
n-$C_{11}H_{23}$	50	135–6	Ethanol	60.1	6.4	2.7	30.8	59.9	6.4	2.7	31.1

TABLE II



R	% Yield	Recrystallization solvent	Elemental analysis					
			Calculated			Found		
			C	H	N	C	H	N
n-C_5H_{11}	26	Methanol	87.9	7.0	5.1	87.4	7.0	5.1
n-C_6H_{13}	17	Methanol	87.8	7.4	4.9	87.7	7.3	4.9
n-C_7H_{15}	31	Methanol	87.7	7.7	4.6	87.4	7.6	4.7
n-C_8H_{17}	26	Ethanol	87.6	8.0	4.4	87.3	8.0	4.6
n-C_9H_{19}	30	Ethanol	87.5	8.3	4.2	87.1	8.2	4.2
n-$C_{10}H_{21}$	27	Ethanol	87.4	8.5	4.1	87.3	8.5	4.1
n-$C_{11}H_{23}$	13	Methanol	87.3	8.7	3.9	87.0	8.5	4.0

EXPERIMENTAL

The preparation of 4-cyano-4'-*n*-octyltolan is illustrative of the general class of 4-cyano-4'-alkyltolans:

4-[1,2-Dibromoethyl-2-(4'-*n*-octylphenyl)]benzonitrile:

4-Cyano-4'-*n*-octylstilbene[2] (24 g, 0.075 moles) in 200 ml. of a glacial acetic acid was heated on a steam bath to give solution. An equimolar quantity of pyridinium bromide perbromide was added portionwise to this solution over a period of 5 minutes. The reaction mixture was allowed to stir at this temperature for 10–15 minutes. The solids which precipitated in cooling the solution to room temperature were filtered and recrystallized.

4-Cyano-4'-*n*-octyltolan:

A solution of 4-[1,2-dibromoethyl-2-(4'-*n*-octylphenyl)]benzonitrile (8.0 g, 0.16 moles) and 1,5-diazobicyclo[5,4,0]undec-5-ene (5.4 g, 0.32 moles) in 25 ml. of dimethylformamide was heated to reflux for $1\frac{1}{2}$ hours. The dimethylformamide was removed under vacuum and the residual oil cooled and recrystallized.

4-[1(or 2)-Bromoethenyl-2-(4'-*n*-pentylphenyl)]benzonitrile:

A solution of 4-(1,2-dibromoethyl-2-(4'-*n*-pentylphenyl)]benzonitrile (1.5 g, 0.0035 mole) and 1,5-diazobicyclo[5,4,0]undec-5-ene (0.6 g, 0.0035 mole) in

20 ml. of dimethylformamide was heated on a steam bath for 15 minutes. The reaction mixture was poured into ice and made acidic with HCl. The precipitate was filtered and recrystallized from ethanol. A crystalline solid m. 63.5–64°C was obtained. It weighed 0.6 g. The nmr spectrum shown in Figure 1 suggested a monobromo compound had been obtained.

Analysis: Cacld. for $C_{20}H_{20}BrN$: C, 67.80; H, 5.69; Br 22.55; N, 3.95:,
Found: C, 67.91; H, 5.79; Br 22.62; N, 3.89;

Microscopy: The transition temperatures were obtained by polarized light, hot stage microscopy using a Mettler FP52 hot stage at a heating rate of 2°/minute.

References

1. J. Malthete *et al.*, *Mol. Cryst. and Liq. Cryst.*, **23**, 233 (1973).
2. R. J. Cox and N. J. Clecak, to be published.
3. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Nash, *Liquid Crystals and Ordered Fluids*, Vol. 2, J. F. Johnson and R. S. Porter, eds. (Plenum Press, 1974), p. 617.
4. W. R. Young, A. Aviram, and R. J. Cox, *Angew Chem.*, **83**, 399 (1971).