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THE TRANSITION TEMPERATURES OF SOME DEUTERIATED LIQUID CRYSTALS

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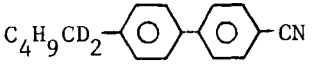
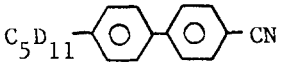
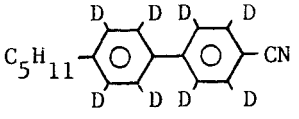
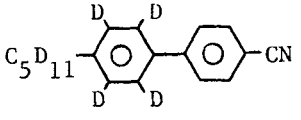
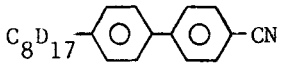
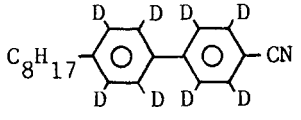
The transition temperatures of eight deuteriated, liquid crystalline derivatives of 4-cyanobiphenyl and four deuteriated liquid crystalline Schiff's bases are reported and compared with the transition temperatures of the corresponding non-deuteriated compounds.

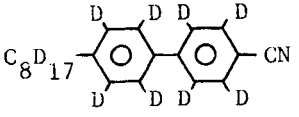
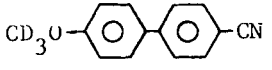
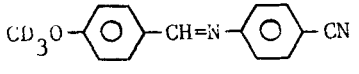
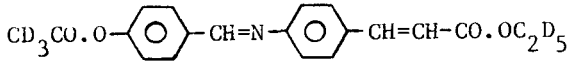
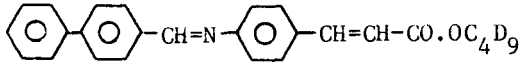
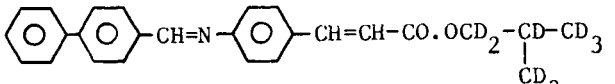
In 1973 a project was initiated to study the molecular structures of various liquid crystalline phases by inelastic neutron scattering. Our part in this work was to prepare the highly deuteriated liquid crystals that would be necessary for this type of physical measurement. During the course of this work, we noted that the liquid crystalline transition temperatures of the deuteriated mesogens differed to small, but measureable extents from the transition temperatures of the corresponding non-deuteriated mesogens. Moreover, these differences were either positive or negative depending upon the liquid crystalline system.

In this communication, we have merely listed, see Table 1, the deuteriated mesogens we have prepared, together with the experimentally observed differences between the transition temperatures of the corresponding deuteriated and non-deuteriated compounds. We feel that these unique data may be useful to those who are concerned with theoretical treatments of liquid crystals.

The crystal-liquid crystal transition temperatures were not affected by deuteriation. Values of ΔT which are less than $0.5^{o}C$ may not be significant. Compounds 1 and 8 were prepared for our own work and compound 4 was prepared for deuteron magnetic resonance studies. The isotopic purity of all the compounds was shown by n.m.r. to be greater than 98%. The purity of compounds 2-7 was shown by g.l.c. to be

TABLE 1 Transition temperatures of deuteriated liquid crystals

Structure of deuteriated mesogen	Compound number	Observed liquid crystalline transition temperatures (°C)	ΔT^*
	*1*	N $\underline{34.8}$ I	+0.1
	*2*	N $\underline{33.7}$ I	−1.0
	*3*	N $\underline{35.3}$ I	+0.6
	*4*	N $\underline{34.3}$ I	−0.3
	*5*	S_A $\underline{33.0}$ N, N $\underline{39.7}$ I	−0.6, −0.9
	*6*	S_A $\underline{34.7}$ N, N $\underline{41.5}$ I	+1.1, +0.9

Structure of deuteriated mesogen	Compound number	Observed liquid crystalline transition temperatures (°C)	ΔT^*
	7	$S_A \xrightarrow{33.0} N$, $N \xrightarrow{39.1} I$	-0.6, -1.5
	8	$[N \xrightarrow{86.0} I]$	-0.25
	9	$N \xrightarrow{120.0} I$	+1
	10	$S_A \xrightarrow{128.0} N$, $N \xrightarrow{159.0} I$	+3, +3
	11	$S_E \xrightarrow{108.0} S_B$, $S_B \xrightarrow{173.0} S_A$ $S_A \xrightarrow{209.0} I$	0, +0.6, +1.5
	12	$S_E \xrightarrow{114.6} S_B$, $S_B \xrightarrow{163.5} S_A$ $S_A \xrightarrow{208.5} N$, $N \xrightarrow{215.5} I$	+0.6, +0.5, +1.1, +0.7

*ΔT = (Transition temperature of deuteriated mesogen) - (transition temperature of non-deuteriated mesogen.)

[ ] Indicates a monotropic transition.

≥99%. The purity of compound *1* was 98%; the impurity in this compound (probably the alkene with side chain $C_3H_7CH{=}CD-$) could have raised the N-I transition temperature by ~0.5°C. Compounds *8-12* were purified by repeated crystallisation until constant transition temperatures were obtained.

The small differences between the transition temperatures of the deuteriated and non-deuteriated compounds could be demonstrated in the following manner. In the case of compound *2*, the temperature of the hot stage which was mounted on a polarizing microscope was set at 34.2°C. A sample of *2* placed in this hot stage would produce the isotropic liquid phase, whereas a sample of non-deuteriated 4-cyano-4'-n-pentyl-biphenyl would remain in the nematic phase.

The values of ΔT are of course very small and it could be argued that such small changes could be due to the presence of impurities. Great care was however taken in purifying all the samples. The corresponding deuteriated and non-deuteriated compounds were prepared by identical synthetic routes and both compounds had very similar g.l.c. purities, where these were measured. Moreover, when a given non-deuteriated mesogen is prepared several times, the variation in N-I temperature is extremely small; in fact a constant N-I value can usually be achieved. All the compounds with the exception of compound *1* had extremely narrow ranges (0.1°C) for the N-I or S_A-I transitions. These factors together with the consistent nature of the results lead us to believe that the effects illustrated in Table 1 (with the exception of compound *1*), are genuine, particularly the sign of ΔT.

Reviewing the results, the following points may be made. It appears that chain deuteriation of a mesogen with a positive dielectric anisotropy ($\Delta\varepsilon$), i.e., compounds *2-8* (neglecting compound *1*), leads to a decrease in the N-I and S_A-N transition temperatures, whereas ring deuteriation of such compounds (i.e., $\Delta\varepsilon > 0$) leads to an increase in these transition temperatures. The only exception to this behaviour is compound *9*. In compounds with $\Delta\varepsilon < 0$, i.e., compounds *10-12*, chain deuteriation leads to an increase in the liquid crystalline transition temperatures.

Although these effects are probably due to the smaller polarisability of deuterium compared with hydrogen, we are not able to explain the data in Table 1, particularly the sign of ΔT.

The synthesis of compound 2 has been published.[1] The syntheses of other deuteriated 4-n-alkyl-4'-cyanobiphenyls will be published elsewhere.[2] The remaining compounds were prepared by normal synthetic routes, starting with commercially available deuteriated reagents.

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References

1 G.W. Gray and A. Mosley, *Mol. Cryst. Liq. Cryst.*, 35, 71 (1976).

2 The synthesis and deuteron magnetic resonance studies of compound 4 have been submitted for publication in *Mol. Phys.*