The Effect of the Terminal Trifluoromethyl Group on Nematic Liquid Crystal Thermal Stability

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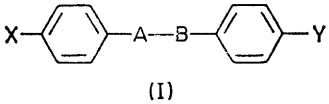
The introduction of a terminal substituent into the molecule of a compound capable of forming liquid crystals enhances the clearing temperature of the nematic phase relative to that of the unsubstituted analogue. The efficiency of the trifluoromethyl group in this respect is assessed relative to that of other groups by incorporating the group in two Schiff's bases. No enantiotropic nematic phase was produced in either case, and ' virtual ' transition temperatures had to be obtained. The low efficiency of the CF_3 group relative to that of other groups is discussed.

LIQUID crystals are quite commonly formed by organic compounds composed of fairly rigid, rod- or lath-shaped molecules. The molecules need not be large or complex, and the requirements are met by simple compounds of general structure (I) in which two *p*-phenylene rings are linked by a central group which frequently involves an unsaturated linkage, *e.g.*, –CH=N–, -C≡C–, –N=N–, *etc.* It has always been found[1] that the *para*-substituents (X and/or Y) enhance the nematic liquid crystal thermal stabilities [defined as the nematic–isotropic liquid (N–I) transition temperatures] relative to that of the unsubstituted compound with one or two terminal hydrogens.



(I)

The relative efficiency order for various terminal groups in promoting nematic thermal stability is well documented[1] and is a very important consideration when planning the synthesis of new liquid crystal materials. It is known that the best terminal substituents for enhancing nematic phase thermal stability are those which both lengthen the molecule and extend the conjugation in the molecule, *e.g.*, groups such as Ph, CN, and NO_2. The least efficient groups are substituents such as fluoro which is small and gives rise to only weak conjugative interactions. However, although the effects can be discussed broadly in terms of enhancement of the anisotropy of molecular polarisability, the detailed arrangement of the terminal groups within the efficiency order for nematic phase thermal stability reflects no consistent trends in the properties of the groups. Usually[1] the order is $Ph > CN > NO_2 > Cl \geqslant Br > CH_3 > I > F > H$.

Terminal substituents are also important in their effect on the dielectric anisotropies (ε_a) of liquid crystal materials. The cyano-group is therefore a very useful terminal group as it produces materials of strongly positive dielectric anisotropy with high nematic phase thermal stability for use in electro-optical displays.

Indeed no satisfactory alternatives to the cyano-group are known, and the commercial availability of simple trifluoromethyl compounds aroused our interest in evaluating the CF_3 group as a terminal substituent in compounds capable of forming liquid crystals. We therefore prepared *N*-(4-n-hexyloxybenzylidene)-4-trifluoromethylaniline (I; X = n-$C_6H_{13}O$, A–B = CH=N, Y = CF_3). This compound melts at 84.5°, but does not show any nematic phase even when the isotropic liquid is rapidly chilled. The analogous compound with Y = CN does form an enantiotropic nematic phase which clears at 101.5°. Thus, the CF_3 group gives a large decrease in nematic phase thermal stability relative to that conferred by the CN group. By mixing the trifluoromethyl compound with known amounts of *N*-(4-ethoxybenzylidene)-4-cyanoaniline [crystal–nematic transition temperature (C–N), 101°; N–I, 128°] and determining the N–I transition temperatures of the mixtures, a phase diagram for the binary system was constructed. The ' virtual ' N–I transition temperature of the trifluoromethyl compound was found, by extrapolation, to be 27°. A similar phase diagram was constructed for *N*-(4-hexyloxybenzylidene)aniline, the unsubstituted analogue of the trifluoromethyl compound with Y = H; the ' virtual ' N–I transition temperature was –52°.

TABLE 1

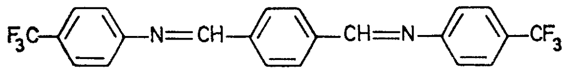
Transition temperatures for the compounds $p\text{-}XC_6H_4N{=}CHC_6H_4OC_6H_{13}\text{-}p$

X	C–N(°)	N–I(°)
CN	56	101.5
CH_3	61.5	73.7
CF_3	84.5	[27]
H	48	[–52]

C = crystal; N = nematic; I = isotropic liquid; [ ] denotes a ' virtual ', monotropic transition.

These results (see Table 1) show that the CF_3 group is considerably more efficient than H for enhancing nematic phase thermal stability (in this case by 79°), but much inferior to CN or CH_3 (by 74.5 and 46.7°, respectively).

An evaluation of the CF_3 group in relation to other terminal groups was next made using a system which is inherently more nematogenic. αα'-Bis-(4-trifluoromethylphenylimino)-*p*-xylene (II) and the analogous compounds with terminal substituents CN, CH_3, and H were prepared.



(II)

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[1] G. W. Gray, ' Liquid Crystals and Plastic Crystals,' eds. G. W. Gray and P. A. Winsor, Ellis Horwood Ltd., Chichester, 1974, vol. 1, ch. 4.1.

Again the trifluoromethyl compound did not show a nematic phase. The compound was found to be immiscible with the cyano and methyl substituted analogues, but was miscible with 4-n-propoxyphenyl 4′-cyanobiphenyl-4-carboxylate (C–N, 146°; N–I, 281°).[2] Data were obtained for various mixtures, and a phase diagram was constructed. A 'virtual' N–I transition temperature of 162° was obtained by extrapolation. A similar phase diagram for (II; H for CF_3) with (II; CH_3 for CF_3) was constructed and the 'virtual' N–I transition temperature of the compound with no terminal substituents was found to be 27°. The results given in Table 2, which includes literature data for related materials, confirm the position of the CF_3 group in the order relative to H, CN, and CH_3, and also locate the group more precisely in the order relative to a range of other substituents. Since the CF_3 group is much better than H (by 135° in this case) and worse than F (by 63° in this case), the order becomes $CN \gg Cl = Br > CH_3 > I > F > CF_3 > H$.

TABLE 2

Transition temperatures for the compounds $p\text{-XC}_6\text{H}_4\text{N=CHC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{X-}p$

X	C–N (°)	N–I (°)	Ref.
CN	220	>295 (decomp)	
CH_3	191	273	
Br	208	288	*a*
Cl	180	288	*a*
I	262	268	*a*
F	151	225	*a*
CF_3	182	[162]	
H	161	[27]	

[a] D. Demus, H. Demus, and H. Zaschke, 'Flüssige Kristalle in Tabellen,' VEB Deutscher Verlag für Grundstoffindustrie; Lepzig, 1974, p. 117.

That the CF_3 group is a more efficient terminal group than H can probably be rationalised in terms of the increased length of the substituted molecule. However, the CF_3 group is a much less efficient terminal group than the smaller CH_3 group. Two factors may be of importance here. First, the larger size of the CF_3 group will result in a broadening of the molecule, thereby reducing the effective lateral attractive forces between molecules in the nematic phase. Secondly, although the CF_3 group will produce a large resultant dipole moment operating along the long molecular axis ($PhCF_3$ has a dipole moment of 8.69×10^{-30} Cm whereas $PhCH_3$ has a dipole moment of 1.33×10^{-30} Cm),[3] the rotating component of this resultant dipole moment at right angles to the long molecular axis, despite its averaging to zero, is capable of producing instantaneous repulsions between neighbouring molecules. Such instantaneous repulsions will be much less significant in the case of the less polar CH_3 group. These factors together may explain the lower nematic phase thermal stability of the trifluoromethyl-substituted compounds compared with the methyl-substituted analogues.

In the case of the cyano-substituted system, the strong axial dipole (PhCN has a dipole moment of 12.59×10^{-30} Cm)[3] is a result of the conjugation of the cyano-group with the phenyl ring system. This produces a larger region of delocalised and polarisable electron density compared with that for the terminally methyl-substituted system. This enhanced anisotropy of polarisability accounts for the greater efficiency of the cyano-group as a terminal group relative to those of all other groups examined, except of course for the phenyl group which enhances conjugation in the molecule, adds length to the molecule and does not produce repulsive dipolar effects.

EXPERIMENTAL

N-(4-*n*-*Hexyloxybenzylidene*)-4-*trifluoromethylaniline*.—This was prepared by heating under reflux for 20 min a mixture of 4-n-hexyloxybenzaldehyde[4] (0.5 g, 0.0024 mol), 4-trifluoromethylaniline (0.35 g, 0.0022 mol) (Fluorochem Ltd.), and ethanol (10 ml) containing one drop of glacial acetic acid. On cooling, the product was filtered off and recrystallised to constant m.p. from ethanol. Related Schiff's bases were prepared in a similar way from 4-cyanoaniline, *p*-toluidine, and aniline.

αα′-*Bis*-(4-*trifluoromethylphenylimino*)-p-*xylene*.— This was prepared in a similar manner, but using more ethanol (30 ml) and twice the molar amount of amine. Related Schiff's bases were prepared similarly from 4-cyanoaniline, *p*-toluidine, and aniline.

Satisfactory elemental analyses were given by all the compounds reported.

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[2] D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, in the press.

[3] A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

[4] J. B. Hartley, M.Sc. Thesis, University of Hull, 1954.