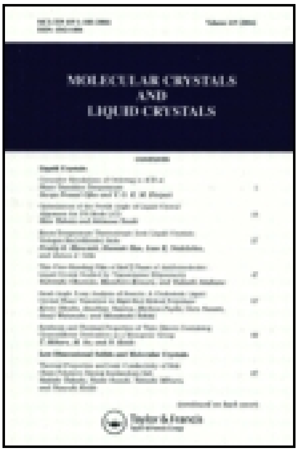

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# Liquid Crystals with a Thiomethyl End Group: Lateral Fluoro Substituted 4-(trans-4-(n-Propyl) Cyclohexylethyl-4′-Thiomethylbiphenyls and 4-n-Alkyl-4″-Thiomethylterphenyls

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# LIQUID CRYSTALS WITH A THIOMETHYL END GROUP: LATERAL FLUORO SUBSTITUTED 4-(*trans*-4-(*n*-PROPYL) CYCLOHEXYLETHYL-4′-THIOMETHYLBIPHENYLS AND 4-*n*-ALKYL-4′′-THIOMETHYLTERPHENYLS.

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Abstract. The synthesis and mesogenic properties of some lateral fluoro substituted 4-(*trans*-4-(*n*-propyl)cyclohexylethyl)-4′-thiomethylbiphenyls and 4-*n*-alkyl-4′′-thiomethylterphenyls are described. Birefringence ($\Delta n$) and dielectric anisotropy ($\Delta\epsilon$) measurements for these compounds are also given and compared with analogous terminal chloro, cyano and methoxy compounds. It is found that the use of a terminal thiomethyl group produces compounds of intermediate $\Delta n$, $\Delta\epsilon$ and clearing point than analogous terminal chloro, methoxy and cyano compounds. The terminal thiomethyl group is also more smectogenic than any of the other three terminal endgroups. In most cases, however, the melting points of the compounds are too high to be of practical use.

## INTRODUCTION.

In the development of novel liquid crystal electro-optical devices, the materials requirements become ever more stringent. It has recently been shown that the performance of a polymer dispersed liquid crystal / active matrix display device can be enhanced by the use of a highly birefringent nematic liquid crystal mixture(1). Lateral fluoro substituted alkylchloroterphenyls(2), *trans*- alkylcyclohexyl ethyl chlorobiphenyls(3) and alkylbiphenyl ethylchlorobenzenes(4) are new materials that are very well suited to PDLC/AMD usage(1), exhibiting moderately low melting points, high birefringence ($\Delta n$) values and a high degree of chemical and photostability.

There are many examples of where the high polarisability of the sulphur atom has been utilised within the molecular structure of a liquid crystal to increase its birefringence(5-7) whilst retaining the mesogenic behaviour. The compounds described below demonstrate the use of the thiomethyl end group to achieve a high Δn value and are compared to analogous chloro, cyano and methoxy compounds.

## EXPERIMENTAL.

Synthesis The compounds reported in this paper were synthesised by standard synthetic organic chemistry procedures involving for example Friedel Crafts acylation, Huang Minlon reductions and boronic acid couplings(8). The synthetic pathways used are shown in figures 1 - 3. The crude materials were purified by flash column chromatography on MERCK 40 - 63 μm silica gel, using petroleum spirit (b.p. 40 - 60°C) and ethyl acetate as the eluant and then recrystallised to >99.5% purity from petroleum spirit (b.p. 80 - 100°C) or 1 - propanol. The materials were analysed for purity by reverse phase high performance liquid chromatography using a Hewlett Packard 1090 instrument equipped with a diode array detector.

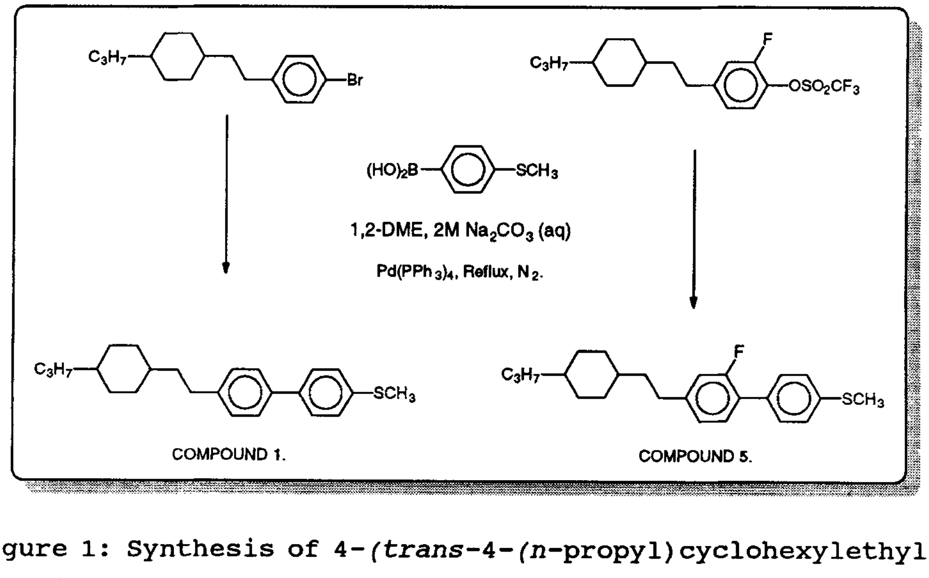


Figure 1: Synthesis of 4-(*trans*-4-(*n*-propyl)cyclohexylethyl)-4′-thiomethyl(fluoro)biphenyls.

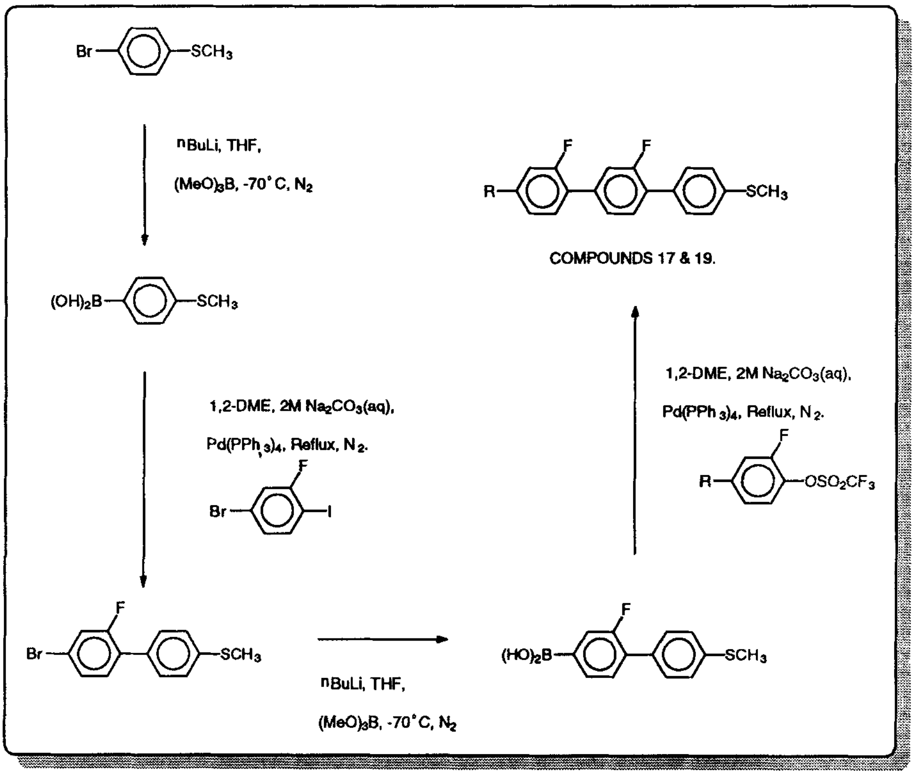


Figure 2: Synthesis of 4-*n*-alkyl-4''-thiomethyl difluoroterphenyls.

<u>Physical Characterisation</u> The structure of the compounds was confirmed by $^1$H NMR spectroscopy using a Jeol PMX 60 SI and G.C. mass spectrometry using a Nermag R1010S quadrupole instrument. Phase transition temperatures were measured using a Perkin Elmer DSC7 differential scanning calorimeter. Phase types were assigned against known standard samples by polarising microscopy using a Mettler FP52 hot stage to control the temperature of the sample. $\Delta n$ and dielectric anisotropy ($\Delta\epsilon$) measurements were made using a 10% w/w solution of the test compound in a chemically related medium $\Delta\epsilon$ mixture MERCK ZLI-4792 ($\Delta\epsilon = 5.1$) at 20°C. Terminal cyano compounds were measured under equivalent conditions in a cyano based host mixture MERCK ZLI-1132 ($\Delta\epsilon = 11.23$). $\Delta n$ was measured

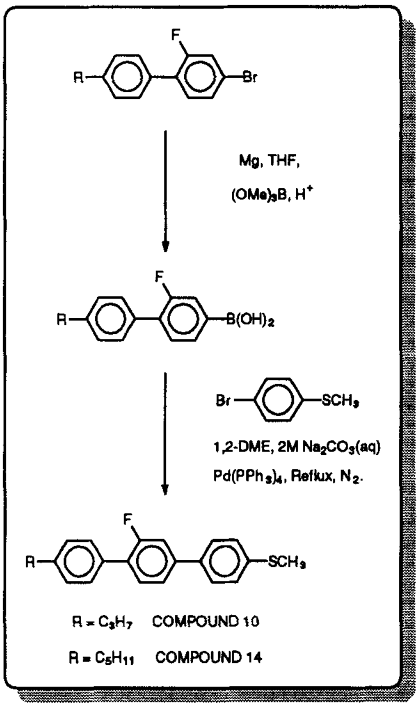


Figure 3: Synthesis of 4-*n*-alkyl-4''-thiomethyl monofluoro terphenyls.

using an Abbé refractometer and Na$_D$ light (589.7 nm.) at 20°C and $\Delta\epsilon$ was measured by an electrical capacitative method at 20°C and 1kHz. The $\Delta n$ and $\Delta\epsilon$ data is, in all cases, obtained from solutions of the compounds in a host nematic liquid crystal mixture at 20°C. Therefore the data refers to how the compound behaves in a liquid crystal mixture rather than being typical for the pure compound. Compounds with a high clearing point will give anomalously higher values than similar related materials of lower clearing point. For this work the mixture values are most appropriate, however it must be recognised that the values, as presented, should not be strictly interpreted as being those of the pure compound.

Molecular modelling Molecular models of the variously substituted 4-*n*-pentyl-2'- fluoro-4''- terphenyls were constructed using NEMESIS V1.1, PC based version (Oxford Molecular Ltd.) and then iteratively calculated to a minimum molecular energy conformer using the COSMIC(9) optimised energy calculation. The molecular energy calculations were performed with the benzene rings of the terphenyl system initially in a co-planar conformation.

## RESULTS AND DISCUSSION.

The mesophase behaviour, $\Delta n$ and $\Delta\epsilon$ measurements are shown in tables 1 - 5.

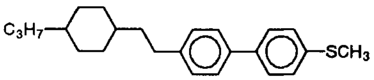
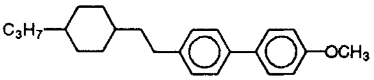
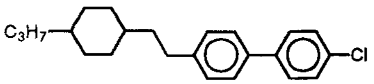
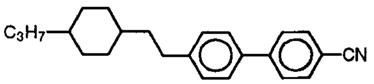
Mesophase behaviour. An initial examination of the mesophase behaviour of compounds **1** - **20** shows that they all possess liquid crystal phases over a wide temperature range. In the majority of compounds, the nematic phase is the most broad and stable phase although some enantiotropic smectic phases are also observed. If the various structural features of the molecules are compared, the following trends are observed:-

1. Effect of terminal group. In all four compound types, altering the end group produces the same effect on clearing point. For a given structural type, an order of increasing clearing point:-

$$-Cl < -SCH_3 < -OCH_3 < CN$$

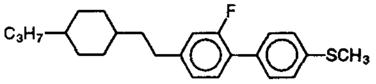
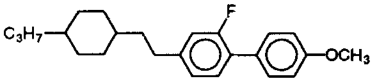
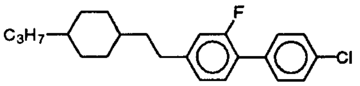
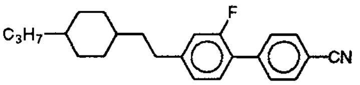
can be assigned. A possible explanation for this order of increasing clearing points and the position of the terminal thiomethyl group within that order is that, with one exception, the polarisability of the end groups increases from chloro to cyano. The exception to this is the methoxy compounds having higher clearing points than the thiomethyl compounds. This exception can be explained by considering the relative bond lengths and angles of the thiomethyl and methoxy groups. The bond lengths of the carbon - sulphur bonds are on average longer than the carbon - oxygen bonds ($sp^3C - S = 1.812Å$; $sp^2C - S = 1.809Å$; $sp^3C - O = 1.416Å$; $sp^2C - O = 1.376Å$)and the C-S-C bond angle is greater than the C-O-C bond

Table 1: Mesophase behaviour and extrapolated physical properties for 4-(*trans*-4-(*n*-propyl) cyclohexylethyl -4'-substituted biphenyls.

| COMPOUND: | MESOPHASE BEHAVIOUR /°C. | Δn | Δε |
|---|---|---|---|
|  **1.** | K 92 $S_A$ 124 N 165 I | 0.217 | +2 |
|  **2.** | K 96 N 175.6 I | 0.198 | +1 |
|  **3.** | K 101.2 N 158 I | 0.197 | +1 |
|  **4.** | K 74 N 188 I | 0.225 | +13 |

angle ($\theta_{CSC}$ = 95.2°; $\theta_{COC}$ = 117.1°) (see figure 4). The net effect of this is that the methyl group in a thiomethyl liquid crystal compound protrudes further away from the side of the mesogenic core than does the methyl group in a methoxy liquid crystal compound. It is effectively acting as a lateral substituent and it is well documented(10,11) that to increase the size of a lateral substitutent in a liquid crystal decreases its clearing point. An examination of tables 1 - 5 also shows that the terminal thiomethyl group is likely to induce a smectic phase in a molecule. A comparison of compounds **9**, **10**, **11** & **12** shows that whereas compounds **10** & **12**, the methoxy and cyano analogues of the propyl monofluoroterphenyl mesogenic unit only display nematic phases, compound **11** , the chloro

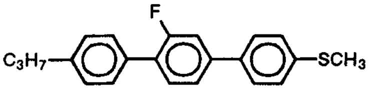
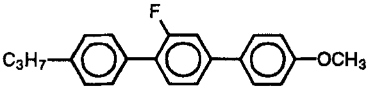
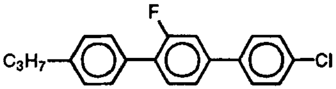
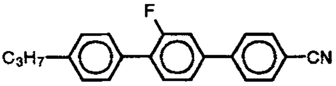
Table 2: Mesophase behaviour and extrapolated physical properties for 2-fluoro-4-(*trans*-4-(*n*-propyl) cyclohexylethyl -4'-substituted biphenyls.

| COMPOUND: | MESOPHASE BEHAVIOUR /°C. | $\Delta n$ | $\Delta \epsilon$ |
|---|---|---|---|
|  **5.** | K 72 N 127 I | 0.197 | +3 |
|  **6.** | K 60 N 143 I | 0.178 | +1 |
|  **7.** | K 72 N 120 I | 0.180 | +5 |
|  **8.** | K 63.1 N 159.7 I | 0.214 | +20 |

analogue exhibits a monotropic $S_A$ phase and compound **9**, the thiomethyl analogue shows enantiotropic $S_B$ and $S_A$ phases. The chloro compounds however usually have the greater smectic phase stability, for example comparing compounds **13** & **15**, the $S_A$ phase is more stable by 18°C in the chloro analogue than in the thiomethyl analogue. An exception to this is compounds **1** & **3**, in which the thiomethyl compound has a greater smectic phase stability by at least 23°C.

2. Effect of lateral fluoro substitution. Modification of the mesogenic core of a liquid crystal molecule by lateral fluoro substitution is a widely studied area(12 - 15). The number and position of lateral fluoro substituents can have a profound effect on the mesogenic phase behaviour of a compound

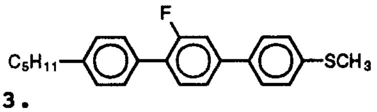
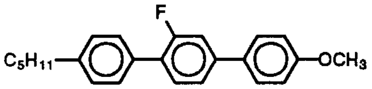
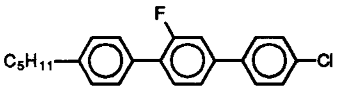
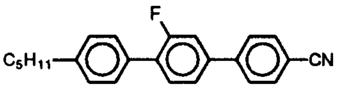
Table 3: Mesophase behaviour and extrapolated physical properties for 4-*n*-propyl-2′-fluoro-4′′-substituted terphenyls.

| COMPOUND: | MESOPHASE BEHAVIOUR /°C. | Δn | Δε |
|---|---|---|---|
|  **9.** | K 100 $S_B$ 108 $S_A$ 112 N 168 I | 0.328 | +3 |
|  **10.** | K 85 N 185 I | 0.296 | +2 |
|  **11.** | K 126 $S_A$ (125) N 163 I | 0.280* | # |
|  **12.** | K 86.2 N 205.4 I | 0.377 | +14 |

* measured from a 5%w/w solution ZLI-4792.
# insoluble at 10%w/w in ZLI-4792.

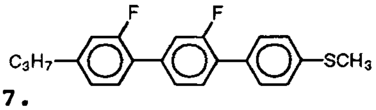
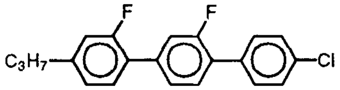
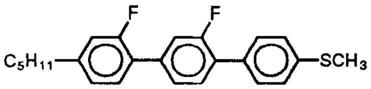
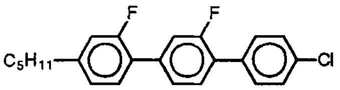
and this has been utilised in many cases to synthesise materials that have broad nematic phases. If compounds **1** and **5** are compared, it is seen that introduction of a lateral fluoro substitutent in an inter-annular position produces a reduction in melting point of 20°C, complete removal of the $S_A$ phase and a reduction in clearing point of 38°C. This is typical for any liquid crystal compound and its fluoro substituted analogue. If compounds **9** & **11** or **17** & **18** are compared it can also be seen that incorporation of a second lateral fluoro substitutent in an inter-annular position again reduces the clearing point relative to a monofluoro substituted and the smectic mesophase stability. The effect on

Table 4: Mesophase behaviour and extrapolated physical properties for 4-*n*-pentyl-2′-fluoro-4′′-substituted terphenyls.

| COMPOUND: | MESOPHASE BEHAVIOUR /°C. | $\Delta n$ | $\Delta\epsilon$ |
|---|---|---|---|
|  **13.** | K 94 $S_A$ 116 N 165 I | 0.304 | +3 |
|  **14.** | K 72 N 177 I | 0.278 | +2 |
|  **15.** | K 96 $S_A$ 134 N 157 I | 0.269 | +5 |
|  **16.** | K 97 N 189 I | 0.343 | +10 |

melting point is less pronounced though. The reasons for these effects on phase behaviour and melting point by lateral fluoro substituents are rationalised firstly by Chan et al(16) and also by Toyne *et al*(17) who found that a lateral fluoro substituent in an inter-annular position increased the inter-annular twisting, which in turn altered the mesogenic phase behaviour. To summarise, the effect of lateral fluoro substitution in terminal thiomethyl compounds is the same as with all other endgroup types, and it can therefore be concluded that there are no specific synergistic effects between the lateral fluoro substituent and the thiomethyl group.

Table 5: Mesophase behaviour and extrapolated physical properties for 4-*n*-alkyl-2,3′-difluoro-4′′-substituted terphenyls.

| COMPOUND: | MESOPHASE BEHAVIOUR /°C. | Δn | Δε |
|---|---|---|---|
|  **17.** | K 104 N 123 I | 0.285 | +8 |
|  **18.** | K 91 N 112 I | 0.260 | +16 |
|  **19.** | K 98 N 121 I | 0.276 | +5 |
|  **20.** | K 60 N 112 I | 0.246 | +12 |

Birefringence measurements. If the birefringence values for the thiomethyl compounds **1**, **5**, **9**, **17** & **19** are compared with their chloro, methoxy and cyano analogues, it can again be seen that there is an order of increasing birefringence for the various end groups. This order is as follows:-

**Cl < $OCH_3$ < $SCH_3$ < CN.**

The reason for this order is that an increasing polarisability of the end group leads to an effective extension of the delocalised system of electrons in the aromatic mesogenic core portion of the molecule. This increases the overall polarisability of the molecule, leading to the more effective retardation of the e-ray of light at visible wavelengths. This results in a very high

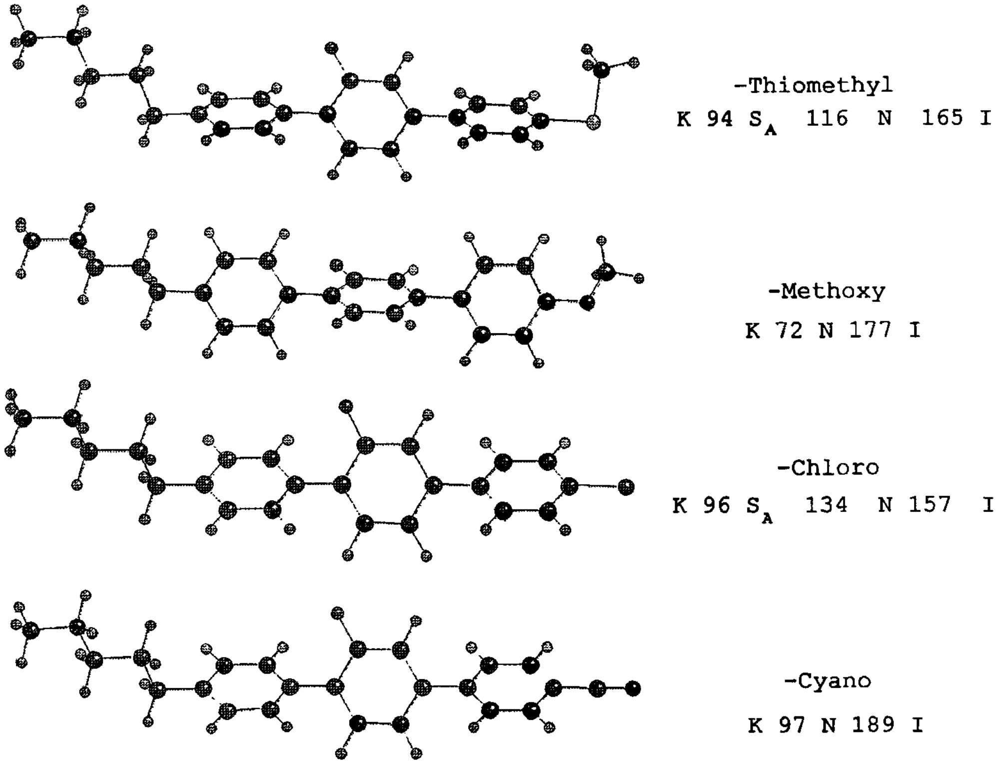


Figure 4.

Molecular Models of 4-n-pentyl-2'-fluoro-4'' substituted 1,1':4',1''-terphenyls

extraordinary refractive index for the molecule, which, according to the standard equation for birefringence:-

$$\Delta n = n_e - n_o$$

will result in a high value of birefringence. If the birefringence values for any given set e.g. compounds **9** - **12** are examined and their ranking of increasing values are compared to the ranking of their increasing clearing points, it can be seen that there is a difference (**-Cl** < **-$SCH_3$** < **-$OCH_3$** < **CN** for the clearing points and **Cl** < **$OCH_3$** < **$SCH_3$** < **CN** for the birefringence values). From this, it can therefore be concluded that the technique of measurement adopted for birefringence (a linear extrapolation of values taken from a solution of the test compound in a host mixture) is a valid one. The reason for this is that if the ranking of values measured for birefringence matched the ranking of values for clearing points, it could be argued that the increasing birefringence was purely a consequence of the higher clearing point of a target compound endowing the guest host mixture with a higher clearing point which would increase the order parameter and therefore the birefringence at a given temperature. The fact that the two orders are different, implies that other factors, such as molecular polarisability also effect the birefringence. A good specific example of this is a comparison of compounds **13** & **14** where although the methoxy compound has the higher clearing point, it is the thiomethyl compound that has the higher $\Delta n$ value.

Dielectric anisotropy If the values of dielectric anisotropy are compared, it can be seen that the terminal thiomethyl group produces a slightly positive dielectric anisotropy in all cases. These values compare in the following order to the other polar end groups:-

$$\mathbf{OCH_3 < SCH_3 < Cl < CN}$$

It is likely that this ranking is a consequence of the dipole moment contributions of the substituted phenyl portion (e.g. thioanisole) of the molecule(18). It has been shown by Pohl and Finkenzeller(14) that the overall molecular dipole moment for a liquid crystal molecule can be derived from a combination of individual dipole moments from various parts of the molecule, and that the dielectric anisotropy is in turn related to this.

## CONCLUSIONS.

The use of the thiomethyl group in a terminal position in a liquid crystal can produce compounds of high birefringence, moderate to high clearing point and slightly positive dielectric anisotropy. Compound **9** was also found by means of a voltage holding ratio test⁽¹⁹⁾ to have the very high stability to light and UV radiation necessary for use in a mixture designed for active matrix applications. The melting points in the majority of cases however are too high for the compounds to be used extensively in mixtures.

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