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# Substituted Terminal Alkyl Groups and Their Prospects in Liquid Crystal Chemistry

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Polar substituents may be attached to the terminal alkyl groups of rodlike mesogens to increase their $\epsilon_\perp$ and to give a positive or negative $\Delta\epsilon$. The mesomorphic behaviour of some biphenyls, phenylcyclohexanes and bicyclohexanes with substituted alkyl groups was studied and compared to that of the corresponding unsubstituted compounds. In the first series no conclusive results could be obtained due to the relatively high melting points and low clearing points of the investigated compounds. In the phenylcyclohexanes and bicyclohexanes, substituents in ω-position were found to enhance the clearing temperature. In contrast, cyano groups in α-position depressed the clearing point. However, this depression is still much less than that caused by the introduction of lateral substituents in the phenyl moieties of the rigid core.

## INTRODUCTION

Mesogens used in display applications are generally rod-like molecules which consist of rigid cores and terminal polar (eg. CN) or nonpolar (eg. alkyl) substituents. Nonpolar groups mainly influence the thermodynamic stability of the mesophase while the polar substituents have a major effect on the dielectric properties.[1] Nematogens with terminal cyano groups are known to have large positive dielectric anisotropy ($\Delta\epsilon$). In twisted nematic (TN) displays, their electro-optic contrast curves have favourable low threshold voltages, but are generally not steep enough to allow high multiplexing rates. Low ratios ($\leq 1$) of $\Delta\epsilon/\epsilon_\perp$ (dielectric constant perpendicular to the optical axis),[2] and of bend to splay elastic constants[3] $k_{33}/k_{11}$ are required for matrix-addressed TN-displays. To improve $\Delta\epsilon/\epsilon_\perp$ of mesogenic nitriles, one of the lateral hydrogen atoms in the aromatic

nucleus has been replaced by a halogen atom or a cyano group.[4] (The effect of such lateral substitution on $k_{33}/k_{11}$ has not yet been explored.) Lateral substituents have also been introduced in terminally nonpolar (dialkyl and alkyl alkoxy) mesogens to give negative values for $\Delta\epsilon$.[5,6] However, the clearing point in all cases is usually depressed by these projecting lateral substituents due to the decrease in geometrical anisotropy and to an increase in the distance between the interacting molecules.[7]

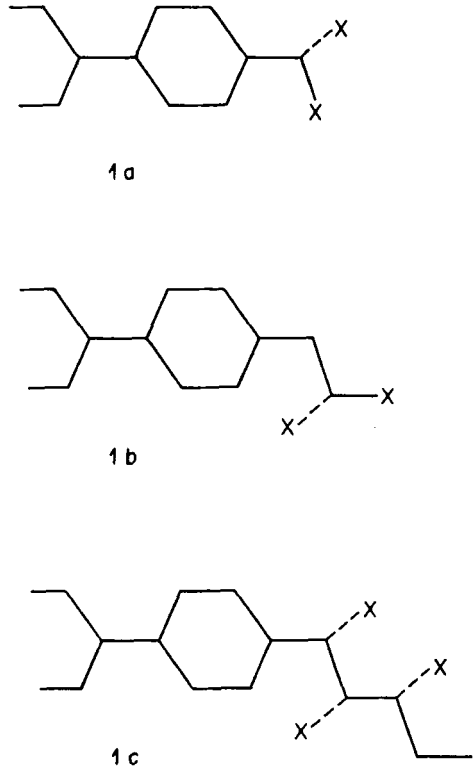



FIGURE 1 Models of rodlike molecules with substituted terminal alkyl groups.

In order to obtain materials with positive or negative $\Delta\epsilon$, large $\epsilon_\perp$ and relatively high clearing points, it may be more favorable to incorporate the polar groups in the terminal alkyl substituents (Figure 1). Such substituents will probably fit better within a cylindrical molecular envelope and do not force the molecules apart. They would therefore be expected to depress the clearing point by only a small amount. Positive $\Delta\epsilon$ can be obtained if the polar group is attached to even numbered terminal methylene groups (Figure 1b) while the other terminal group is alkyl. In this case $\epsilon_\perp$ will be larger than if the polar group was directly attached to the rigid core due to the possible rotation of the polar group out of the long molecular axis. The higher the number of methylene units which separate the polar group from the rigid core, the greater the degree of rotational freedom will be. The value of $k_{33}/k_{11}$ of such mesogens is expected to be smaller than that of the corresponding compounds with cyano groups directly attached to the rigid core, due to the flexibility of the alkyl chain[8] and to the low degree of association in aliphatic nitriles.[9] A positive $\Delta\epsilon$ can also be obtained when the terminal substituent at the other end of the rigid core has a larger dipole moment than that of the polar group attached to the alkyl chain. In case of 1a and 1c (Figure 1), negative $\Delta\epsilon$ is to be expected provided that the other terminal substituent is nonpolar.

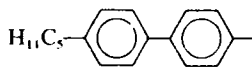
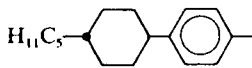
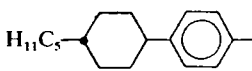
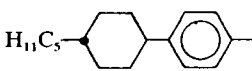
In this publication the influence of attaching polar substituents to the terminal alkyl groups of rodlike mesogens on their mesomorphic behaviour is described.

## RESULTS AND DISCUSSION

The thermal data of some biphenyls and phenylcyclohexanes with substituted terminal alkyl groups are given in Table I. Those of the bicyclohexyl derivatives are given in Table II.

In the biphenyl series, the polar substituents raised the melting point so that no mesomorphic behaviour could be observed in the investigated compounds. In the phenylcyclohexanes, the 2-bromoethyl derivative 6 did not show any mesomorphic behaviour down to $-25$°C, while the corresponding propyl derivative 8 has a N-I transition ($\vartheta_{ni}$) at $-11.2$°C. In contrast, the 2-cyanoethyl group (compd. 9) enhanced the clearing point by 40°C compared to that of compd. 8. However, it is still 27°C lower than that of the 4-trans-pentylcyclohexyl-4-benzonitrile. This is probably due to the lower degree of association in aliphatic nitriles.[9] Replacing one of the α-hydrogens in

Influence of substituted alkyl groups on the mesomorphic behaviour of biphenyls and phenylcyclohexanes

| | | C | S | S | N | I | |
|---|---|---|---|---|---|---|---|
| 1) |  | 49 | – | – | – | 10 | |
| 2) | —$CH_2CH_2I$ | 84 | – | – | – | . | |
| 3) | —$C_3H_7$ | −18 | – | 47.8 | – | . | |
| 4) | —$CH_2CH_2CN$ | 66.5 | – | – | – | 10 | |
| 5) | —$CH_2CH_2OH$ | 72 | – | 112.5 | – | . | |
| 6) |  | 30 | – | – | – | . | No mesophase down to −25°C |
| 7) | —$CH_2CH_2I$ | 36.2 | – | – | – | . | No mesophase down to −10°C |
| 8) | —$CH_2CH_2CH_3$ | −12.7 | – | – | −11.2 | 11 | |
| 9) | —$CH_2CH_2CN$ | 44.8 | – | – | (28.3) | 12 | |
| 10) | —$CH_2CH_2OH$ | 29 | 59.2 | 73.4 | – | . | |
| 11) |  | −0.8 | – | (−8) | (−5.0) | 11 | |
| 12) | $H_9C_4CH$ <br> \| <br> CN | 34.0 | – | – | – | . | |
| 13) |  | 54.2 | – | – | (42.9) | 13 | |
| 14) | —$CO(CH_2)_3F$ | 57.6 | – | (50.0) | (55.8) | . | |

C = crystalline, S = smectic, N = nematic, I = isotropic. Values given in brackets represent monotropic phases. A dot shows the existence of a phase transition while a dash indicates that the corresponding phase is missing. All values are given in °C.

TABLE II

Influence of substituted alkyl groups on the mesomorphic behaviour of bicyclohexanes


| | $R^1$ | $R^2$ | C | S | S | N | I |
|---|---|---|---|---|---|---|---|
| 15) | $C_3H_7$ | $CH_3$ | . 7 | – | . 25.7 | – | 11 . |
| 16) | | $CH_2Br$ | . 44.4 | – | (. 36.1) | – | . |
| 17) | | $CH_2CN$ | . 54 | – | . 75.7 | – | . |
| 18) | | $C_3H_7$ | . 64.2 | – | . 81.8 | – | 11 . |
| 19) | | $CH_2CH_2CN$ | . 13 | . 30 | . 99.0 | – | 12 . |
| 20) | $C_5H_{11}$ | $CH_2Br$ | . 39 | – | . 45 | . 51 | . |
| 21) | | $CH_2OH$ | . 65 | – | . 130 | – | . |
| 22) | | $CH_2CN$ | . 56.5 | – | . 82.6 | – | . |
| 23) | | $CH_2CH_3$ | . −8 | – | . 76.1 | – | . |
| 24) | | $CH_2CH_2Br$ | . 46.0 | – | . 47.8 | . 67.9 | . |
| 25) | | $CH_2CH_2CN$ | . 9 | . 30 | . 108.8 | – | 12 . |
| 26) | | $CH_2CH_2OH$ | . 44 | – | . 152.8 | – | . |
| 27) | | $C_5H_{11}$ | . 40 | – | . 110.4 | – | 13 . |
| 28) | | $CHC_4H_9$ \| CN | . 35 | – | . 80.0 | – | . |

For symbols see Table I.

the 4,4′-dipentyl-phenylcyclohexane by a cyano group (compd. 12) led to the disappearance of the mesophase. However, a fluorine atom in ω-position (compd. 14) enhanced the clearing point by 13°C compared to that of the unsubstituted compd. 13. Therefore, it seems that polar substituents in ω-position raise the clearing point while those in α-position depress it.

Replacing one of the hydrogen atoms of the methyl group in the bicyclohexane 15 by a bromine atom increased its smectic-isotropic transition temperature ($\vartheta_{si}$) by 10°C. The same substituent decreased the clearing point of the ethyl derivative 23 by 8°C and induced a nematic phase on top of the smectic one. A similar observation was made for compound 20. Attaching a cyano substituent instead of the bromine to the methyl group (compd. 17) strongly enhanced $\vartheta_{si}$. However, it is still intermediate between those of the methyl and propyl derivatives 15 and 18. It is also 4°C lower than $\vartheta_{ni}$ of the 4-*trans*-propyl-4′-*trans*-cyanocyclohexylcyclohexane.[14] The pentyl homologue 22 has a clearing point which is 7°C higher than that of the ethyl derivative 23. Introduction of the same substituent in an ethyl group (compd. 19) also enhanced the clearing point. The $\vartheta_{si}$ of compd.

19 is 17°C higher than that of the propyl derivative 18 which has the same molecular length. It is also 14°C higher than that of the 4-trans-pentyl-4'-trans-cyanocyclohexylcyclohexane.[14] The same observation is also made in the pentyl homologue 25. In contrast, the introduction of a cyano group in an α-position (compd. 28) lowered $\vartheta_{si}$ by 30°C. Therefore, it can be said that polar substituents attached to the terminal alkyl groups of rodlike molecules in ω-positions enhance the clearing point, while those in α-position depress it. However, this depression is still much less than that caused by the introduction of lateral substituents in phenyl groups.

In general, it can be concluded that the introduction of polar groups in the terminal alkyl substituents leads to mesogens with relatively high clearing points. These compounds can be useful as components of nematic mixtures with positive $\Delta\epsilon$ suitable for matrix-addressed TN-displays or of those with negative $\Delta\epsilon$.

## EXPERIMENTAL

The mesomorphic properties were investigated by differential thermal analysis (DTA) and polarizing microscopy using a PE-DSC 2 and a Leitz Orthoplan. The microscope was equipped with a Mettler FP 5/52 heating stage which was cooled by means of a cold nitrogen gas stream. The transition temperatures were optically measured at 0.2°C/min heating rate, while the differential thermal analysis was carried out at a rate of 5°C/min. Crystal smectic and smectic smectic transitions which were optically difficult to observe were detected by DTA. Only the melting points of the stable crystalline phases are given.

### Compounds 5, 10, 21, and 26

A solution of the corresponding acid (0.1 mol) in dry THF was added dropwise to a suspension of $LiAlH_4$ (10 g) in 100 ml THF at 0°C. The mixture was then refluxed for 1 h, poured on cold dilute HCl and the product extracted in ether. The product was crystallized from ethanol.

### Compounds 6, 16, 20 and 24

Bromine (0.12 mol) was added dropwise to a suspension of $P(Ph)_3$ (0.12 mol) in dry $CH_3CN$ at 0°C and the mixture stirred for 30 min at r.t. To this suspension, a solution of the corresponding alcohol

(see above) in $CH_3CN$ was added dropwise and the mixture stirred for 15 min. The solvent was then distilled off and the reactants heated for 30 min at 130°C. $CH_2Cl_2$ and $H_2O$ were added to the cooled mixture and the organic phase poured into hexane to precipitate the triphenylphosphine oxide. The raw product was purified by chromatography on silica gel with toluene as an eluent.

### Compounds 2 and 7

A mixture of $(PhO)_3P$ (30 m mol) and $CH_3I$ (40 m mol) was gradually heated to 120°C (2 h), then cooled to r.t. A solution of the corresponding alcohol (20 m mol) was then added and the mixture stirred at r.t. for 4 h. The reaction mixture was poured on ice, extracted with ether and the organic phase washed and dried. The product was purified by chromatography on silica gel with toluene-hexane 1:2 as an eluent. Recrystalization was achieved in ethanol.

### Compounds 17 and 22

A mixture of the corresponding bromide 16, or 21 (20 m mol) and powdered KCN (4 g) in 50 ml DMSO was stirred at 100°C for 2 h, then poured onto $H_2O$. The product was extracted in ether, filtered through a short silica gel column with toluene as an eluent, and crystallized from ethanol.-IR ($CHCl_3$) 2240 (CN).

### 1-(4-Fluorobutanoyl)-4-trans-(4-pentylcyclohexyl)benzene 14

A mixture of 1-bromo-4-chlorobutane (0.2 mol) and KF (0.4 mol) was heated at 120°C in 100 ml diethylene glycol for 6 h. The resulting 1-chloro-4-fluorobutane was purified by fractional distillation (B.p. 115°C).

A solution of the above prepared 1-chloro-4-fluorobutane (20 m mol) in dry ether was added dropwise to a stirred suspension of Mg (20 m mol) in ether, and the reaction mixture stirred for 30 min at r. t. To the resulting Grignard reagent, a solution of 4-*trans*-pentylcyclohexyl-4-benzonitrile (20 m mol) in ether was added. The reaction mixture was refluxed for 4 h, then worked up. The product was purified by chromatography on silica gel with toluene as an eluent followed by crystallization from ethanol.

### Compounds 12 and 13

The corresponding ketone[11] (20 m mol) and 2,4,6-tri-isopropylbenzene-sulfonyl hydrazide (TPSH) (25 m mol) were stirred together in

30 ml THF at r.t. for 2 h. After distilling off the solvent, the residue was redissolved in 30 ml $CH_3OH$ and KCN (60 m mol) was added. The reaction mixture was refluxed for 2 h, after which the solvent was driven off. The product was extracted in $CH_2Cl_2$, washed and dried. It was purified by chromatography over silica gel with $CH_2Cl_2$-hexane 2:3 as an eluent. - IR.($CH_2Cl_2$) 2230 (CN).

### 4-Pentyl-4'-propyl-biphenyl 3

This product was prepared by catalytic (Pd/C) hydrogenation of 4-propyl-4-valeroyl biphenyl in ethanol.

### 4-trans-Ethyl-4'-trans-pentylbicyclohexane 23

Hydrazine hydrate (80%) (70 m mol) and KOH (0.1 mol) were added to a solution of 4-*trans*-acetyl-4'-*trans*-pentylbicyclohexane[11] in 30 ml diethyleneglycol and the mixture was heated under reflux for 2 h. Water was then distilled off the reaction mixture until its temperature rose to 195°C. The mixture was kept at this temperature for 4 h, then cooled and poured onto water (100 ml). The product was extracted in ether and crystallized from ethanol.

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