Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: Maged A. Osman (1985): Molecular Structure and Mesomorphic Properties of Thermotropic Liquid Crystals. III. Lateral Substituents, Molecular Crystals and Liquid Crystals, 128:1-2, 45-63

To link to this article: http://dx.doi.org/10.1080/00268948508082187

Mol. Cryst. Liq. Cryst., 1985, Vol. 128, pp. 45–63
0026-8941/85/1282–0045/$20.00/0

Printed in the United States of America

Molecular Structure and Mesomorphic Properties of Thermotropic Liquid Crystals. III. Lateral Substituents

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(*Received November 14, 1984*)

The effect of lateral substituents on the type and thermodynamic stability of the mesophases shown by terminally polar and nonpolar rod-like mesogens is described. Lateral substituents both sterically force the interacting molecules apart and also hinder the packing of the molecules in a layered structure, thus suppressing smectic order and favouring the nematic phase. The nematic → isotropic transition temperature, ϑ_{ni} decreases with increasing van der Waals volume, V_ω of the lateral substituent, irrespective of its dipole moment, due to the increase in intermolecular distance r. The relationship between ϑ_{ni} and V_ω is non-linear because the repulsive and attractive forces are different functions of r. The depression in ϑ_{ni} depends not only on V_ω of the substituent, but also on its position and on the structure of the rigid core. In aromatic nitriles, lateral substituents with $+M$ effect in an *ortho* position with respect to the terminal cyano group, hinder the molecular association and therefore, lower the clearing point and increase $\epsilon_\parallel$.

INTRODUCTION

Thermotropic rod-like mesogens are geometrically anisotropic molecules which by definition have more or less cylindrical rigid cores. For practical reasons, such as lowering the melting point, enhancing the clearing point, acquiring certain dielectric properties . . . .etc., terminal substituents are usually attached to one or both ends of the rigid core. A number of molecular theories which describe the properties of nematogens have been put forward and were recently reviewed by M. A. Cotter.[1,2] However, none of the existing theories is able to quantitatively describe all the physical properties of me-

sogenic molecules. Therefore, synthetic chemists designing new molecules have to depend on simple (qualitative) correlations between the macroscopic properties and molecular structure.

A correlation between the structure of the rigid core and the mesomorphic behaviour of rodlike mesogens has been recently proposed.[3] The rigid cores of mesogens usually consist of two or more cyclic units (alicyclic, aromatic or heterocyclic) linked directly by covalent bonds or by diatomic linkages (eg. —CH_2CH_2—, —CH_2O—, —COO—). The stereo-chemistry of the rigid core was found to strongly influence the type of mesophase formed as well as its thermodynamic stability. This was attributed to the effect of steric factors on the packing of the molecules, and the intermolecular separation. The influence of polar and nonpolar terminal substituents on the type and stability of the mesophase has also been described.[4] They can increase the polarizability of the molecule, lead to molecular association or increase the intermolecular separation, thus strongly affecting the thermodynamic stability of the mesophase. The necessity of considering the stereo-chemistry and electronic structure of the rigid core to which the substituents are attached, when discussing the influence of the latter was emphasized.

For special reasons, such as increasing $\epsilon_\perp$ (dielectric constant across the long molecular axis), the rigid cores sometimes also carry lateral substituents in addition to terminal ones. The influence of lateral substituents on the clearing point was previously reviewed by G. W. Gray.[5] Recently, there has been an increasing interest in nematogens with large $\epsilon_\perp$ and quite a number of new laterally substituted mesogens have been synthesized. This allows a better understanding of the relation between the structure of laterally substituted mesogens and their mesomorphic properties.

In the following discussion an attempt is made to correlate the mesomorphic behaviour of laterally substituted rod-like molecules with their structures. Until quite recently[6] lateral substituents were exclusively attached to the aromatic nuclei of the rigid core. Therefore, the discussion will be limited to this type of molecule.

RESULTS AND DISCUSSION

Since terminal polar groups can lead to molecular association which influences the type and stability of the mesophase,[4,7-9] it is necessary to discuss the effect of lateral substituents on the mesomorphic behaviour of terminally polar and nonpolar mesogens separately. For

simplicity, polar mesogens are limited here to molecules whose rigid cores carry a terminal cyano group, while the nonpolar ones are restricted to those with terminal alkyl and/or alkoxy groups.

Terminally Nonpolar Mesogens

W. Weissflog and D. Demus[10] have shown that the introduction of lateral alkyl substituents in 1,4-bis-(4-substituted-benzoyloxy)-benzenes lowers their clearing points. With increasing length of the lateral alkyl chain, the clearing points decreased down to convergence temperatures. Thus a methyl group lowered the clearing point of the bis-benzoyloxy benzene by ~ 40°C, an ethyl group by ~ 80°C and a propyl group by ~ 100°C.

The intermolecular repulsive forces as well as the attractive forces (especially the dispersion forces) are known to influence the thermodynamic stability of the mesophase.[3] The molecular interaction energy (E) strongly depends on the intermolecular distance (r). Lateral alkyl groups in the extended *trans* conformation sterically force the inteacting molecules apart and increase r, thus lowering the clearing point. Long alkyl chains can assume gauche-and anti-conformations, and adapt themselves to the ordered rigid core matrix. Therefore, the increase in r would not be expected to be proportional to the number of carbon atoms in the alkyl chain. Furthermore, the interaction energy is a function of $1/r$,[6] while the overlap energy is proportional to $1/r$.[12] Thus, a linear relationship between the clearing point and the number of carbon atoms in the lateral alkyl chain is not to be expected.

TABLE I

Dipole moments and van der Waals volumes of the substituents

X	$^{\mu}C_6H_5X$ $D_{(ref.\ 12)}$	V_{ω} $Å_{(ref.\ 13)}$
F	−1.47	5.8
Cl	−1.59	12.0
CH_3	0.37	13.7
Br	−1.57	14.4
CN	−4.05	14.7
NO_2	−4.01	16.8
NH_2	1.53	10.5

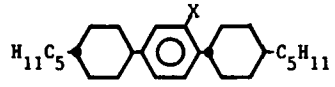
μ = dipole moment, V_{ω} = Van der Waals volume

To study the effect of the volume and polarity of lateral substituents on the mesomorphic behaviour of anisotropic molecules, 1,4-bis-(4-trans-pentylcyclohexyl)-benzene was chosen as the parent mesogen. This molecule is a hydrocarbon consisting of a phenyl group symmetrically substituted in the 1,4-positions by 4-*trans* pentylcyclohexyl groups. The three cyclic units of the rigid core are directly linked by covalent bonds i.e. there are no linkages which could affect the polarity or the geometry of the molecule. Its large geometrical anisotropy and high clearing point allows the introduction of bulky lateral substituents without destroying the long range order. The 2,3,5 and 6 positions in the aromatic moiety are identical in every sense; avoiding the formation of isomers on substitution. Unflexible substituents with definite volumes and different polarities were introduced in this molecule. Their dipole moments[12] (μ) range from 1.5D to -4.1D and their van der Waals volumes[13] (V_ω) vary from 5 Å to 17 Å (Table I) In this context V_ω is considered to be a better indication of r rather than the van der Waals radii which have been used by many authors.

The mesomorphic behaviour of the laterally substituted derivatives 2–8 is compared to that of the parent compound 1 in Table II. The nematic isotropic transition temperatures (ϑ_{ni}) are plotted against V_ω of the substituents in Figure 1. As can be seen, ϑ_{ni} decreases with increasing V_ω of the lateral substituent irrespective of the dipole moment. All the points (except that of the nitro group)

TABLE II

Mesomorphic properties of laterally substituted 1,4-bis(4-*trans*-pentylcyclohexyl)-benzene



	X	C		S		N		I	
1)	H	•	50	•	196	—		•[11]	
2)	F	•	61.0	•	79.2	•	142.8	•	mosaic and homeotropic texture
3)	Cl	•	46.1	—		•	96.1	•	no smectic phase down to −15°C
4)	CH_3	•	55.5	—		•	86.5	•	no smetic phase down to 25°C
5)	Br	•	40.5	—		•	80.8	•	no smectic phase down to 0°C
6)	CN	•	62.8	(•	43.1)	•	79.5	•	fan-shaped texture
7)	NO_2	•	51.2	—		•	57.0	•	no smectic phase down to 25°C
8)	NH_2	•	67	•	163	—		•	mosaic and homeotropic texture

C = crystalline, S = smectic, N = nematic, I = isotropic. Values given in brackets represent monotropic phases and 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.

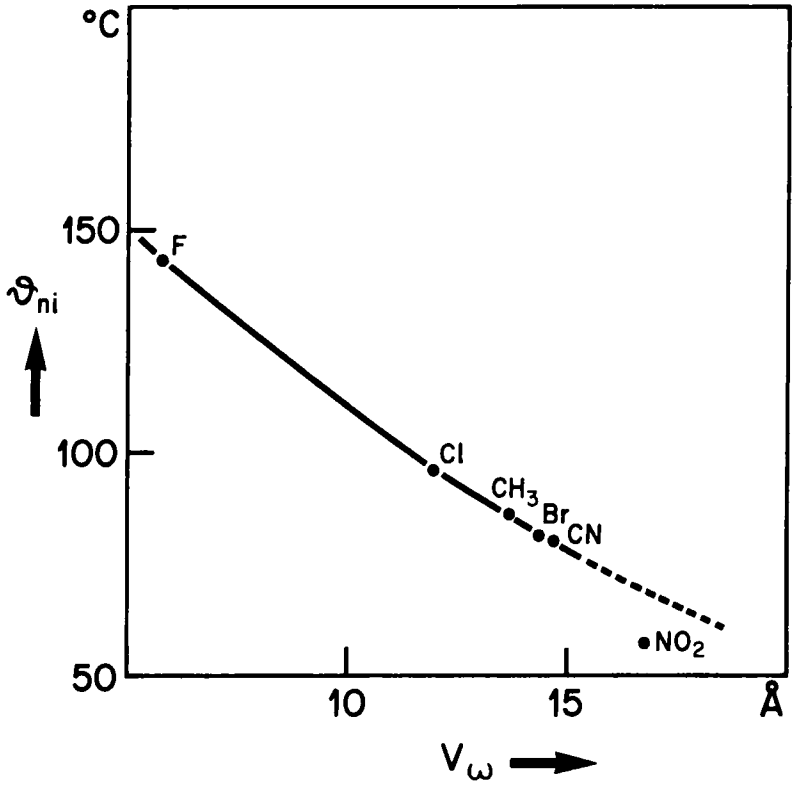


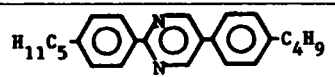
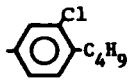
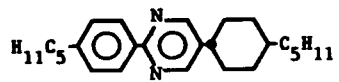
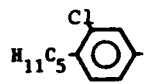
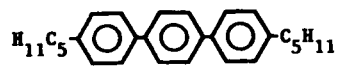
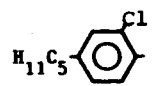
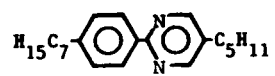
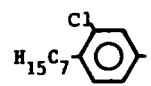
FIGURE 1 ϑ_{ni} of laterally substituted 1,4-bis-(4-*trans*-n-pentyl-cyclohexyl)-benzenes as a function of the van der Waals volume of the substituents.

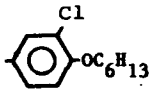
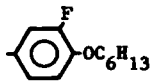
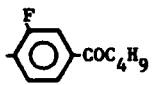
lie on a smooth diverging curve, which indicates that the dipole attractive forces play a minor role compared to that of the dispersive forces. Similar results were obtained by D. Demus *et al*[13] for the derivatives of 1,4-bis- (4-hexylbenzoyloxy) benzene substituted in the 2-position. It is known that both dispersion and overlap energies decrease with increasing intermolecular distance. (However, the first is proportional to $1/r^6$ while the latter is a function of $1/r^{12}$.) Therefore, the intermolecular potential energy (u) levels out with increasing r. Since the clearing point is a function of u, it is to be expected that ϑ_{ni} will show a similar behaviour as long as the mesophase is thermodynamically stable i.e. as long as the chemical potential of the mesophase is lower than that of the isotropic and crystalline phases.

It is also interesting to note the effect of lateral substituents on the type of mesophase formed. At high temperatures, the small fluorine

TABLE III

Influence of lateral substituents on the mesomorphic behaviour of different mesogens

		C	S	N	I
9)		• 106.4	• 185.2	—	•[15]
10)		• 111.3 •	—	(• 102.7)	•[15]
11)		• 39.5 •	• 189.2 •	—	•
12)		• 33.4 •	• 121.2	—	•
13)		• 192 •	• 213 •	—	•[16]
14)		• 56.1 •	—	• 60.2	•
15)		• 30.6 •	• 47.7	—	•[15]
16)		• 35.5 •	—	—	•[15]

17)		•	82	•	84	—		•[15]
18)		•	1.7	—		•	11.1	•[15]
19)		•	37.9	(•	35.3)	(•	36.0)	•[15]
20)		•	56.3	(•	50.9)	•	63.5	•
21)		•	41.4	—		•	44.5	•

atom disturbs the packing of the molecules in layers, thus destabilizing the smectic order, and favouring the less-ordered nematic phase. Larger substituents eliminate the layered structure completely and replace it by a nematic order. However, a monotropic smectic phase appears in the nitrile 6 and a quite stable one is observed in the amine 8. This is probably due to the increased intermolecular interactions in these compounds (increased polarizability) and the relatively small V_ω of the amino group. Therefore, it can be said that the repulsive (steric) and attractive forces arising from the lateral substitution influence the type and stability of the mesophase. The higher the order in the smectic phase of the unsubstituted parent compound and the stronger the attractive forces between the molecules, the larger the volume of the lateral substituent must be in order to be able to eliminate the layered structure.

It should be emphasized that the influence of lateral substituents on the mesomorphic behaviour of terminally nonpolar mesogens described above represents only general trends. In fact, these effects are strongly dependent on the nature of the rigid core to which the substituents are attached, as can be seen from Table III. For example the introduction of a chloro substituent in the diphenyl pyrimidine, 9 replaced the smectic phase by a nematic one and decreased the clearing point by ~80°C. The introduction of the same substituent in compd. 11, where one of the phenyl groups of the diphenyl pyrimidine is replaced by a cyclohexyl moiety was not able to change the smectic order. The clearing point however, was decreased by ~ 70°C. In case of the phenyl pyrimidine 16 which has a shorter rigid core, no mesophase could be observed at all although the unsubstituted parent compd. 15 has a reasonable S-I transition temperature (ϑ_{si}). Chlorination of the alkyl/alkoxy biphenyl 17 led to a nematic phase with a clearing point which is ~70°C lower that ϑ_{si} of the parent compound. No smectic phase could be detected in the chlorobiphenyl 18, even on supercooling the melt to −20°C. The smaller fluoro substituent (compd. 19) decreased the clearing point of the same molecule by ~50°C and a very short nematic phase of 1°C was observed on top of the smectic one. The same substituent caused a depression of ~20°C only in the clearing point of compd. 20 and the smectic phase was totally suppressed. No smectic phase could be detected in compd. 21 on supercooling its melt to 25°C.

In mesogens whose rigid cores consist of covalently bonded phenyl groups, lateral substituents in the 2 and 2′ positions increase the ground state torsional angle between the cyclic units.[17] This increase in torsional angle affects the packing density of the molecules and

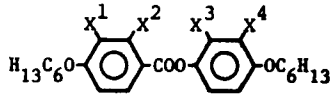
therefore, has an influence on the type of mesophase formed as well as an additionally depressing effect on the clearing point. This is clearly seen in the mesomorphic behaviour of compd. 14. The chloro substituent which lowered the clearing points of compds. 9 and 11 by 70–80°C had a dramatic effect on the mesomorphic properties of the terphenyl 13. The smectic phase was replaced by the less-ordered nematic one and the clearing point was decreased by ~150°C. No smectic phase could be observed on supercooling the melt of compd. 14 down to 25°C.

These data emphasize that the net effect of a lateral substituent on the type and thermodynamic stability of the mesophase is a result of its effect on the subtle balance between the intermolecular attractive and repulsive forces. The increase in the intermolecular distance r, resulting from the lateral substitution depends not only on V_ω of the substituent, but also on the stereochemistry of the rigid core. The interaction energy depends on r as well as on the polarizability of the molecules, which can be affected by the lateral substitution. Therefore, in some cases a small fluoro substituent is able to destroy the layered structure of the smectic phase and replace it by a nematic one. In other instances not even a chlorine atom is able to produce this effect. The clearing point is depressed in all cases by the presence of lateral substituents, but to different extents depending on the nature of the substituent and the structure of the rigid core.

The position of the substituent also plays an important role in determining the stability of the mesophase as can be seen from Table

TABLE IV

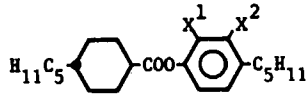
Influence of the substituent position on the mesomorphic behaviour of phenyl benzoates



	X^1	X^2	X^3	X^4	C		S		N		I
22)	H	H	H	H	•	64.5	—		•	90	•[18]
23)	F	H	H	H	•	65.5	—		•	70	•[19]
24)	H	F	H	H	•	39	—		•	68	•[19]
25)	H	H	H	F	•	42	•	66	•	72	•[19]
26)	Cl	H	H	H	•	74	—		—		•[19]
27)	H	Cl	H	H	•	34	—		(•	29)	•[19]
28)	H	H	Cl	H	•	31.5	—		•	44	•[19]
29)	H	H	H	Cl	•	36	•	41	•	53.5	•[19]

TABLE V

Influence of the substituent on the mesomorphic properties of phenyl cyclohexane carboxylates



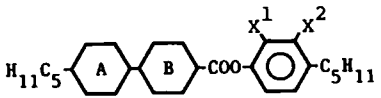
	X^1	X^2	C	S	N	I
30)	H	H	• 36.0	(• 29.0)	• 48.0	•[20]
31)	F	H	• 17.5	—	• 36.5	•[21]
32)	H	F	• 27.5	(• 18.7)	(• 26.3)	•[21]

IV. The clearing points of the chloro phenylbenzoates 26–29 are generally lower than that of the unsubstituted ester 22 and are strongly dependent on the position of the chlorine atom. This is in contrast with the behaviour of the fluoro derivatives 23–25 (smaller substituent), which have the same ϑ_{ni} irrespective of the position of the lateral substituent. However, their ϑ_{ni} is also ~20°C lower than that of the unsubstituted ester 22. In case of the cyclohexane carboxylates 31 and 32 (Table V), the situation is different. The clearing point of compd. 31 is ~10°C higher than that of compd. 32, and the nematic phase is favoured. The clearing points of the fluorophenyl esters are 12°C and 22°C lower than that of the unsubstituted ester 30. These results indicate that the position of the substituent can also affect the mesomorphic behaviour, depending on the stereochemistry of the rigid core and V_ω of the substituent. This is probably because the increments in r due to the lateral substituent can be different if the positions are not sterically equivalent.

The effect of lateral di-substitution on the mesomorphic behaviour of esters is shown in Table VI. In the case of the fully aromatic compound 33, the introduction of a lateral cyano group in the *ortho* position with respect to the carboxyl group, decreased the clearing point by ~70°C and suppressed the smectic phase. The introduction of a second cyano group slightly enhanced the clearing point. For the phenyl ester of cyclohexyl benzoic acid 36, mono substitution decreased ϑ_{ni} by ~50°C, while di-substitution (compd. 38) decreased it by ~ 70°C. In both cases the smectic phase was suppressed. In the esters of the phenyl cyclohexane carboxylic acid, the dicyano phenyl ester, 41 had a higher clearing point (~20°C) than the monocyano derivative and the smectic phase reappeared. For the esters of cyclohexyl cyclohexane carboxylic acid, mono-substitution decreased ϑ_{ni} by ~30°C only. A second cyano group did not appreciably affect

TABLE VI

Influence of lateral cyano groups on the mesomorphic behaviour of phenyl benzoates and phenyl cyclohexane carboxylates



	A	B	X^1	X^2	C		S		N		I	
33)	phenyl	phenyl	H	H	•	95	•	152	•	176	•	[22]
34)			CN	H	•	85	—		•	105	•	[23]
35)			CN	CN	•	99	—		•	112.5	•	[24]
36)	cyclohexyl	phenyl	H	H	•	99	•	135	•	172	•	[25]
37)			CN	H	•	69.5	—		•	123	•	[26]
38)			CN	CN	•	106.1	—		(•	101.6)	•	[27]
39)	phenyl	cyclohexyl	H	H	•	77	•	113.2	•	127.7	•	
40)			CN	H	•	60.8	—		•	64.5	•	
41)			CN	CN	•	110.5	(•	87.5)	(•	87.7)	•	[27]
42)	cyclohexyl	cyclohexyl	H	H	•	38	•	176.8	•	190.1	•	
43)			CN	H	•	61.5	—		•	159.6	•	
44)			CN	CN	•	87.7	•	154.2	•	168.6	•	[27]

the clearing point, but enhanced the formation of the smectic phase which had been suppressed by the first lateral substituent. This indicates that a second substituent (in homo-substitution) has little effect on the clearing point, since it fills in the space and does not increase the intermolecular separation. However, it can influence the van der Waals forces and consequently the type of mesophase formed. The effect of the second substituent is more pronounced when the two positions are not sterically or electronically equivalent.

It remains to be remarked that mesogens carrying lateral polar substituents show a much lower degree of association (correlation factor $g = 0.91$)[28] than those which have terminal polar groups ($g = 0.4 - 0.6$),[9] as indicated by dielectric measurements. Such molecular correlations are known to influence the clearing point.[4] The reason for the smaller degree of association is probably the smaller charge separation, the larger intermolecular distance and the diminished rotational symmetry in laterally substituted compounds.

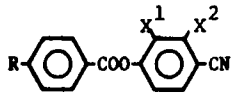
Terminally polar mesogens

The major effect of terminal polar groups attached to mesogenic molecules is observed in the dielectric properties. However, they also influence the type and thermodynamic stability of the mesophase due to the increased molecular interactions and due to the molecular association which affect the packing of the molecules. As a result, terminal cyano groups attached to aromatic moieties usually lead to nematic phases with high clearing points.[4,7-9] When the cyano group is attached to an alicyclic unit, the situation is different, due to the low degree of association and due to the small potential energy barrier ($-\Delta G°$) between the isotropic *aa* and the anisotropic *ee* conformers.[4,29]

In aromatic nitriles, the mesomeric effect ($-M$) of the polar cyano group leads to the build up of charges at the ends of the mesomeric system giving rise to molecular association. In addition to their steric effects' lateral substituents with $+M$ effect (eg. halogen) *ortho* to the terminal cyano group further reduce the charge separation. Thus, they decrease the molecular association and consequently lower the clearing point. For example, the introduction of a small substituent such as a fluorine atom *ortho* to the cyano group of 4-cyanophenyl benzoates reduces ϑ_{ni} by ~35°C (Table VII). While the same substituent in the *meta* position has practically no effect on the clearing point. It should be recalled here that ϑ_{ni} of the nonpolar fluorophenyl benzoates are ~20°C lower than that of the unsubstituted compound

TABLE VII

Effect of lateral fluoro substituents on the mesomorphic behaviour of 4-cyanophenyl benzoates



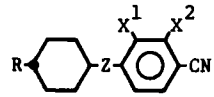
	R	X¹	X²	C		N		I
45)	C_3H_7	H	H	•	103.5	(•	51.5)	•[32]
46)		F	H	•	55.5	(•	51)	•[32]
47)		H	F	•	70	(•	18)	•[30]
48)	C_4H_9	H	H	•	66.8	(•	42.5)	•[33]
49)		F	H	•	46.5	(•	42)	•[32]
50)		H	F	•	14	(•	7)	•[30]
51)	C_5H_{11}	H	H	•	63.4	(•	56.8)	•[33]
52)		F	H	•	53.5	•	55	•[32]
53)		H	F	•	30	(•	20)	•[30]

irrespective of the position of the fluorine atom (Table IV). Therefore, the large reduction in ϑ_{ni} of the aromatic nitrile by the *ortho* fluorine atom can be attributed to the suppression of the molecular association. The hinderance of the molecular association leads also to an increase in $\Delta\epsilon$ (the dielectric anisotropy)[31] i.e. to the regain of $\Delta\epsilon$ which was lost by the anti-parallel correlation.

The same effect is observed in the cyclohexyl derivatives (Table VIII). The introduction of a fluoro substituent *ortho* to the cyano

TABLE VIII

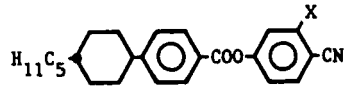
Effect of lateral fluoro substituents on the mesomorphic behaviour of 4-cyanophenyl cyclohexanes and 4-cyanophenyl cyclohexane carboxylates



	R	Z	X¹	X²	C		N		I
54)	C_5H_{11}	—	H	H	•	31	•	55	•[34]
55)			H	F	•	17	(•	11)	•[35]
56)	C_7H_{15}	—	H	H	•	30	•	59	•[34]
57)			F	H	•	39.7	•	58.6	•[35]
58)	C_5H_{11}	COO	H	H	•	47.2	•	79.4	•[36]
59)			H	F	•	40	•	42	•[32]
60)			F	H	•	75.5	•	93.5	•[32]

TABLE IX

Effect of substituent volume on the clearing point of terminally polar mesogens



	X	C		N		I
61)	H	•	111	•	225	•[25]
62)	F	•	91	•	195	•[37]
63)	Cl	•	82	•	142	•[38]
64)	CN	•	85.2	•	143.9	•[35]

group of the phenyl cyclohexane 54 decreased the clearing point by 44°C, while the same substituent in the *meta* position (compd. 57) had no effect. In the cyclohexane carboxylate 58, a fluorine atom in the *ortho* position lowered ϑ_{ni} by 37°C while the same substituent in meta position increased it by 14°C. The same substitution in the corresponding nonpolar ester (Table V) depressed ϑ_{ni} by 22°C and 12°C respectively. This again shows the effect of suppressing the molecular association on the clearing point.

The effect of increasing V_ω of the lateral substituent on the clearing point of polar mesogens is shown in Table IX. The clearing point decreases with increasing V_ω of the lateral substituent in a similar manner to that observed in nonpolar mesogens. Therefore, it can be concluded that in polar mesogens, lateral substituents may hinder the molecular association and have an additional effect on the clearing point beside those described for nonpolar mesogens.

EXPERIMENTAL

The mesomorphic properties were investigated by differential thermal analysis and polarizing microscopy using a PE-DSC 2 and a Leitz Orthoplan equipped with a Mettler FP 5/52 heating stage. The heating stage was cooled by means of a cold nitrogen gas stream. The transition temperatures were measured under the microscope 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 DSC. Only the melting points of the stable crystalline phases are given.

General method of halogenation

A solution of the necessary amount of halogen (Cl_2 or Br_2) in CCl_4 was added dropwise to a stirred suspension of iron powder in a solution of the unsubstituted product in CCl_4 at 0°C. The degree of halogenation was checked by g.l.c. and kept below 70% to prevent the production of dihalogenated products.

2-Chloro-1,4-bis-(4-trans-n-pentyl-cyclohexyl)-benzene 3

Compound 1 was chlorinated according to the above described method and the raw product was purified by chromatography on silica gel using hexane as an eluent. It was crystallized from ethanol.

2-Bromo-1,4-bis-(4-trans-n-pentyl-cyclohexyl)-benzene 5

Compound 1 was brominated and the product purified by chromatography as described above, followed by crystallization from ethanol. ^{1}H-NMR($CDCl_3$):0.87 ppm (*t*, J = 6 Hz, 6 H, 2 CH_3); 1-2.1 ppm (*m*, 34 H, 16 CH_2 and 2 CH next to CH_2); 2.4 and 2.8 ppm (br. *t*, J = 10 Hz, 2 H, CH next to arom. moiety); 7.1 ppm (m, 2 H, arom. CH); and 7.3 (br., 1 H, arom. CH).

2-Methyl-1,4-bis-(4-trans-n-pentyl-cyclohexyl)-benzene 4

$TiCl_4$ (0.3 mol) was added to a cooled (-10°C) solution of compd. 1 (0.1 mol) in 100 ml $CHCl_3$. Dichloromethyl methyl ether (0.3 mol) was added dropwise to the solution with stirring. The mixture was stirred at room temperature overnight and then poured on to ice. The organic phase was separated, washed neutral and dried over $MgSO_4$. The product obtained by distilling off the solvent was filtered through a short silica gel column with toluene as a solvent. The aldehyde obtained was catalytically hydrogenated in ethyl acetate using 10% Pd/c as a catalyst (room temperature, normal pressure). The raw product was filtered through silica gel column with hexane as a solvent, then crystallized from isopropanol.

2-Cyano-1,4-bis-(4-*trans*-n-pentyl-cyclohexyl)-benzene 6

CuCN (0.2 mol) was added to a solution of (0.1 mol) compd. 5 in 100 ml N-methyl-2-pyrolidone. The mixture was heated at 180°C for 3 h with stirring, then cooled to room temperature and added to a solution of 29 g $FeCl_3$ and 200 ml conc. HCl in 500 ml H_2O. After stirring the mixture at 60°C for 30 min, it was cooled to room tem-

perature and extracted with CH_2Cl_2. The organic phase was washed neutral and dried over $MgSO_4$. The raw product obtained by distilling off the solvent was filtered through silica gel with toluene-hexane (1:9) as a solvent. The product was crystallized from ethanol.—IR (CH_2Cl_2): 2220 (CN).

2-Nitro-1,4-bis-(4-*trans*-n-pentyl-cyclohexyl)-benzene 7

A mixture of 2 ml conc. nitric acid, 6 ml conc. sulfuric acid and 20 ml glacial acetic acid was added dropwise to a stirred suspension of 10 m mol compound 1 in an acetic acid–acetic anhydride mixture at −10°C. The reaction mixture was stirred for one more hour, warmed up to room temperature and then worked up. The resulting nitro compound was purified by chromatography on silica gel with toluene-hexane (1:2) as an eluent.

2-Amino-1,4-bis-(4-*trans*-n-pentyl-cyclohexyl)-benzene 8

To a solution of 5 m ml compd. 7 in 40 ml ethyl acetate-ethanol mixture (1:1), 0.2 g Pt/C 10% was added and the mixture hydrogenated at room temperature under normal pressure.—IR ($CHCl_3$): 3370, 3450 (NH_2).

2-Fluoro-1,4-bis-(4-trans-n-pentyl-cyclohexyl)-benzene 2

Equimolar amounts of conc. HCl and $NaNO_2$ were added to a cooled (0–5°C) solution of the amine 8 in THF with stirring. An excess of fluoroboric acid was then added dropwise to the diazonium chloride solution. The precipitated diazofluoroborate was filtered off, washed with cold fluoroboric acid and cold methanol. The well dried diazofluoroborate was then mixed with dry sea sand, and decomposed by heating at 250°C under reduced pressure. The fluoro compound 2 was directly distilled, and crystallized from ethanol.

2-(4-n-pentyl-phenyl)-5-(4-*trans*-n-pentyl-cyclohexyl)-pyrimidine 11

Butyl iodide, 17.5 m mol was added dropwise to a stirred suspension of Mg 20 m mol in dry ether, and the reaction mixture was refluxed for 30 min. A solution of 15 m mol 2-(4-cyano-phenyl)-2-(4-trans-n-pentyl-cyclohexyl-pyrimidine (Roche) in dry THF was added dropwise to the Grignard reagent. The reaction came to an end after refluxing the mixture for 1 h, and was then worked up. The resulting ketone was crystallized from ethanol, and was reduced by heating with hydrazine hydrate 40 m mol and KOH 40 m mol in diethylene

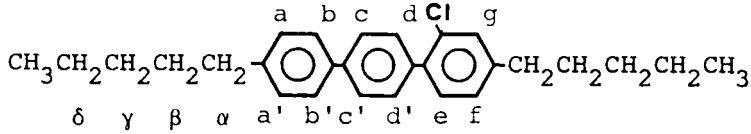
glycol at 135°C for 2 h. Water was then distilled off until the temperature increased to 195°C, and the mixture was kept at this temperature for another 4 h. The cooled reaction mixture was diluted with water, and extracted with ether. Compound 11 was obtained by evaporating the dry neutral ethereal solution. The raw product was filtered through a short silica gel column using toluene as a solvent, and crystallized from ethyl acetate.

2-(3-Chloro-4-n-pentyl-phenyl)-5-(4-trans-n-pentyl-cyclohexyl)-pyrimidine 12

This product was prepared from compd. 11 by the previously described general method of halogenation using $AlCl_3$ as a catalyst. The product was purified by filtration through silica gel with hexane-toluene (9:1) as a solvent, followed by crystallization from ethanol.

1-(2-Chloro-4-n-pentyl-phenyl)-4-(4-n-pentyl-phenyl)benzene 14

The ketone obtained by the action of butyl magnesium bromide on 4-cyano-4″-n-pentyl terphenyl (BDH) was chlorinated as described before to give a mixture of two products (3:1). The mixture was catalytically hydrogenated in ethyl acetate at room temperature and normal pressure using Pd/C 10% as a catalyst. The main product was isolated by chromatography on silica gel (1:100) with hexane as an eluent and crystallized from ethanol. ^1H - NMR ($CDCl_3$): 7.4 - 7.7 ppm (m, 6 H, b, b′, c, c′, d, d′); 7.15 - 7.35 ppm (m, 4 H, a, a′, e, g); 7.1 ppm (dd, 1 H, f); 2.62 and 2.60 ppm (2t, 4 H, α - CH_2); 1.6 ppm (m, 4 H, β - CH_2); 1.1 - 1.5 ppm (m, 8 H, γ- and δ-CH_2); 0.9 ppm (t, 6 H, CH_3)



The number of aromatic protons indicates that the product is a monochloro derivative, thus two of the phenyl groups should exhibit AA′BB′-spin systems. The single aromatic proton at 7.1 ppm belongs to the chlorinated phenyl group and shows a large and a small coupling (J = 8 and 1.5 Hz). Therefore, it must have neighbouring protons in *ortho* and *meta* positions i.e. it is in the *para* position to the chlorine atom. The chemical shift of 7.1 ppm indicates that this proton is *ortho* to the alkyl group. Therefore, the chloro substituent was assigned

meta to the pentyl group. This assignment is confirmed in other similar products.

Compounds 20 and 21

These products were obtained by the action of butyl magnesium bromide on the corresponding nitriles[34,35] and were crystallized from ethanol.

Compounds 40, 42 and 43

These products were prepared by esterification of the appropriate acids with the appropriate phenols. The esters were purified by crystallization from ethanol.

References

1. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **97**, 29 (1983).
2. M. A. Cotter, *Phil. Trans. R. Soc. London*, **A309**, 127 (1983).
3. M. A. Osman, *Z. Naturforsch.*, **38a**, 693 (1983).
4. M. A. Osman, *Z. Naturforsch.*, **38a**, 779 (1983).
5. G. W. Gray, in "Liquid Crystals and Plastic Crystals" (Ellis Horwood, Chichester, 1974), vol. 1, p. 125.
6. R. Eidenschink, G. Haas, M. Römer and B. Scheuble, *Angew. Chem.*, **96**, 151 (1984).
7. Hp. Schad and M. A. Osman, *J. Chem. Phys.*, **75**, 880 (1981).
8. W. H. de Jeu, *Phil. Trans. R. Soc. London*, **A309**, 217 (1983).
9. Hp. Schad, and M. A. Osman, *J. Chem. Phys.*, **79**, 5710 (1983).
10. W. Weissflog and D. Demus, *Crystal Res. and Technol.*, **18**, 21 (1983); **19**, 55 (1984).
11. R. Eidenschink, L. Pohl, M. Römer and F. del Pino, European patent disclosure EP 0 030 277 (1981).
12. V. I. Minkin, O. A. Osipov and Y. A. Zhadnov, "Dipole Moments in Organic Chemistry," (Plenum, N.Y., 1979), p. 91.
13. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
14. D. Demus, A. Hauser, Ch. Selbmann and W. Weissflog, *Crystal Res. and Technol.*, **19**, 271 (1984).
15. M. A. Osman and T. Huynh-Ba, *Z. Naturforsh.*, **38b**, 1221 (1983).
16. H. Schubert, H. Lorenz and R. Franke, *Z. Chem.*, **6**, 337 (1966).
17. L. D. Field and S. Sternhell, *J. Am. Chem. Soc.*, **103**, 738 (1981).
18. R. Steinsträsser, *Z. Naturforsch.*, **27b**, 774 (1972).
19. T. Gunjima, Y. Nakagawa and Y. Masuda, *Reports Res. Lab. Asahi Glass Co.*, **32**, 87 (1982).
20. H. J. Deutscher, R. Laaser, W. Dölling and H. Schubert, *J. Prakt. Chemie*, **320**, 191 (1978).
21. G. W. Gray, C. Hogg and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **67**, 1 (1981).
22. R. Steinsträsser and F. del Pino, German Patent disclosure DEOS 2 450 088 (1974).
23. X. J. Hong, M. J. Ge, X. M. Zhao, Z. R. Fen and Z. J. Liu, *Mol. Cryst. Liq. Cryst.*, **99**, 81 (1983).
24. S. M. Kelly and T. Huynh-Ba, *Helv. Chim. Acta*, **66**, 1850 (1983).

25. R. Eidenschink, *Kontakte (Merck) 1/79*, 15 (1979).
26. R. Dabrowski, J. Dziaduszek, T. Szczucinski, and Z. Raszweski, *Mol. Cryst. Liq. Cryst*, **107**, 411 (1984).
27. M. A. Osman and T. Huynh-Ba, *Mol. Cryst. Liq. Cryst.*, **92**, 57 (1983).
28. Hp. Schad, *21. Bunsen Kolloq.*, Berlin (1983).
29. M. A. Osman and T. Huynh-Ba, *Helv. Chim. Acta.*, **67**, 959 (1984).
30. M. Sasaki, H. Takatsu, H. Sato, T. Shimamura, and K. Toriyama, German Patent disclosure DEOS **3** 241 822 (1983); *Mol. Cryst. Liq. Cryst.*, **109**, 169 (1984).
31. Hp. Schad and S. M. Kelly, *J. Chem. Phys.*, **81**, 1514 (1984).
32. S. M. Kelly, *Helv. Chim. Acta*, **67**, 1572 (1984).
33. A. Boller and H. Scherrer, German Patent disclosure DEOS 2 306 739 (1973).
34. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Agnew. Chem.*, **89**, 103 (1977).
35. M. A. Osman and T. Huynh-Ba, *Mol. Cryst. Liq. Cryst.*, **82**, 331 (1983).
36. H. J. Deutscher, F. Kuschel, S. König, H. Kresse, D. Pfeiffer, A. Wiegeleben, J. Wulf and D. Demus, *Z. Chem.*, **17**, 64 (1977).
37. M. Sasaki, H. Takatsu and H. Sato, German Patent disclosure DEOS 3 339 216 (1984).
38. Y. Hsu, German Patent disclosure DEOS 3 334 054 (1984).