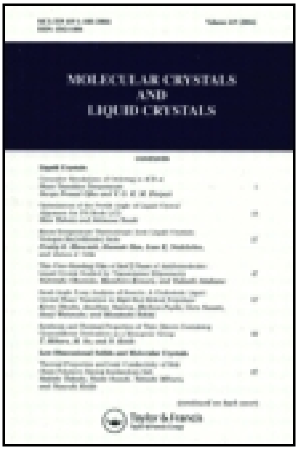

Molecular Crystals and Liquid Crystals

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Molecular Structure and Phasef Transition of Thermotropic Liquid Crystals

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Molecular Structure and Phase Transition of Thermotropic† Liquid Crystals

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This paper will present some empirical trends concerning the relations between molecular structure and phase transitions of thermotropic liquid crystals, ending up with suggestions for the molecular design of low-melting liquid crystal materials with broad nematic ranges. This involves the following aspects: (1) factors inhibiting the appearance of a mesophase, (2) factors leading to monotropic mesophases, (3) factors favoring the formation of low-melting liquid crystal materials and (4) factors influencing the range of the mesophase.

These factors are not only related to the configuration, conformation, and geometrical anisotropy of the molecule, but also to the polarity and polarizability of the molecule.

The mutual effect of the electronic and the stereochemical factors will also be discussed.

INTRODUCTION

In the past few decades, molecular physicists and theoretical chemists have made great efforts to investigate the quantitative relationship between molecular structure and phase transition behavior for thermotropic liquid crystals. As a result, some approximate relations between the clearing point of liquid crystals (T_{NI}) and their molecular polarizability ($\Delta\alpha$), transition order parameter (S_{NI}), transition enthalpy (ΔH_{NI}), transition entropy (ΔS_{NI}), and geometrical anisotropy (L/D), etc., have been derived,[1] among which the Maier-Saupe molecular model based on the mean field approximation of molecular statistical theory is most well known.[2] Although a number of phase transition behaviors of liquid crystal materials, such as (1) the effect of $\Delta\alpha_{CX}$

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†Presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

of C—X bonds (X = various terminal groups) on T_{NI}, (2) the odd-even effect on the T_{NI}-m curve (m = number of carbon atoms in the terminal groups), and (3) the general trend of T_{NI} change with the increase of m, have been accounted for satisfactorily with this approximation, serious deviations of calculated T_{NI} values from the experimental values have also been reported.[1] Recently the modified Maier-Saupe approximation of de Jeu[3] and Kimura,[4] which incorporates the concept of molecular repulsive forces and the so-called "excluded volume" have made encouraging progress in this field. Nevertheless, the application of the above-mentioned quantitative approximations by organic chemists in their work involving the molecular design of new liquid crystal materials appears to be quite limited, because (1) the important nature of T_{CN} in the molecular design of liquid crystals cannot be calculated from these equations and (2) the physical and geometrical parameters required in these calculations are not readily available.

The method of approximate quantitative estimation of T_{NI} values by Knaak *et al.*[5] seems more practical for the liquid crystal molecular designers in spite of the average deviation of around 9° C. However, this procedure also suffers from being unable to estimate T_{CN} and it is not applicable to the important categories of nematic liquid crystals without central linkages, e.g., the biphenyls and the phenylcyclohexanes. Therefore, empirical trends regarding phase transition behavior and molecular structure of thermotropic liquid crystals still prove helpful to the liquid crystal molecular designers, at least for the time being.

1 Some structural features affecting the probability of mesophase formation

The formation and thermal stability of mesophases represent quite a complex and delicate situation involving the interaction and counterbalance of the thermal disturbances of the molecules in a given temperature range with the intermolecular Van der Waals forces, which in turn are functions of various structural factors, both electronic and steric, and it is the sum of these structural factors that determine the strength of the Van der Waals forces and the thermal behavior of the mesophase (Figure 1).

In the azomethine series, some short and bulky polar terminal groups have been proved unfavorable for the formation of a mesophase and are not recommended in the molecular design of liquid crystal materials. This is presumably due to the smaller length-breadth ratio of the molecule and hence weaker intermolecular VDW forces, together with the higher melting points arising from the presence of strongly polar groups (Table I).[6]

The presence of two short n-alkyl groups at both terminal positions in this series also proves unfavorable, because the polarizability anisotropy seems to be too small to generate the intermolecular VDW forces required for the existence of a mesophase (Table II).

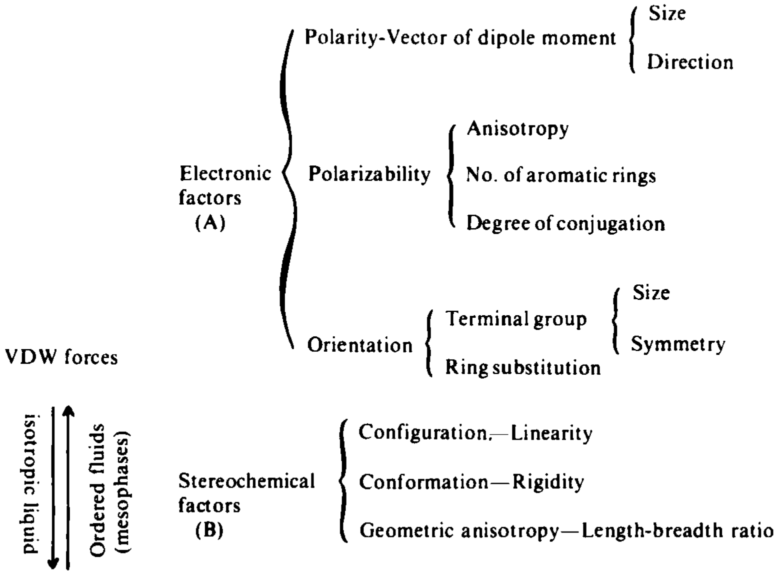
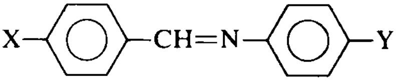


FIGURE 1 Thermal disturbance—associated with temperature rise after melting.

On the other hand, the effect of ring substitution in this series appears somewhat complicated, since it depends upon the nature and the site of orientation of the substituents (Table III).[7] While an OH group at position *Z* inhibits the appearance of the mesophase, the *Z'*—OH stabilizes a liquid crystal phase, presumably due to formation of a six-membered ring with the nitrogen atom, through hydrogen bonding. Meanwhile a methoxy group, either at po-

TABLE I

Short, bulky, polar terminal groups

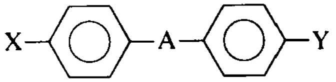


X	Y	mp (°C)
—OCH$_3$	—Br	120
—OCH$_3$	—NO$_2$	125
—OCH$_3$	—OSO$_2$CH$_3$	158–161
—OCH$_3$	$-O\overset{\overset{O}{\|}}{C}CH(CH_3)_2$	100
—OCH$_3$	$-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\|}}{C}CH_3$	164–8

TABLE II

Factors inhibiting the formation of a mesophase

Short *n*-alkyl groups at both terminal positions



A	X	Y	mp (°C)	Ref
—CH=N—	CH_3	n-C_4H_9	12	7
—CH=N—	CH_3	CH_3	92	8
—CH=N—	C_2H_5	CH_3	49	8

sition Z or at position Z' of the ring, gives an unfavorable effect on the formation of a mesophase, obviously due to the increase in molecular breadth and therefore the corresponding reduction in lateral VDW forces.

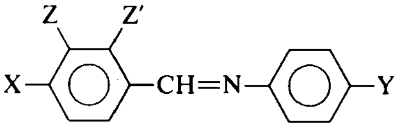
However, even with two unfavorable terminal groups, such as two short *n*-alkyl groups, the mesogenic effect of the central bridge must be brought into consideration as shown in Table IV.[7]

The effect of the structure of the parent core on the phase transition behavior of compounds with identical terminal groups but different parent cores is apparent from Table V.[7]

The 2,6-disubstituted biphenylene system appears to be a poor parent core

TABLE III

Effects of ring substitution

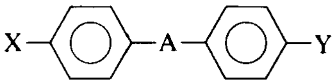


X	Z	Z'	Y	mp (°C)	CP* (°C)
CH_3O	H	H	n-C_4H_9	21	47
CH_3O	OH	H	n-C_4H_9	70	
CH_3O	H	OH	n-C_4H_9	37	59[9]
CH_3O	H	H	$OOCCH_3$	81	108
CH_3O	CH_3O	H	$OOCCH_3$	107	
CH_3O	H	H	$OOCC_3H_7$	50	109
CH_3O	H	CH_3O	$OOCC_3H_7$	88-90	
CH_3O	H	OH	$OOCC_3H_7$	75	104

*CP = clearing point

TABLE IV

Influence of bridge linkage



A	X	Y	mp (°C)	CP (°C)	Ref
$-CH{=}N-$	C_2H_5	CH_3	49		8
$-\overset{\overset{O}{\frown}}{N{=}N}-$	C_2H_5	CH_3	37	71	10
$-N{=}N-$	n-C_3H_7	n-C_3H_7	82		11
$-\overset{\overset{O}{\frown}}{N{=}N}-$	n-C_3H_7	n-C_3H_7	66	(61)*	11

*( ) represents a monotropic transition.

for mesogens, probably due to the comparatively small length-breadth ratio of the molecule, as well as to the poorer molecular linearity. Also, the strained, rigid, flat core seems to contribute to the higher melting points of the series, which might be considered unfavorable for mesophase formation in this particular series. However, when one or two more benzene rings are incorporated into the 2,6-positions of the biphenylene series, normal mesomorphism appears (Table VI).[7]

TABLE V

Effects of bridging linkage

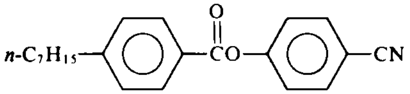
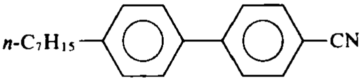
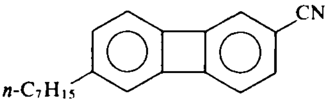
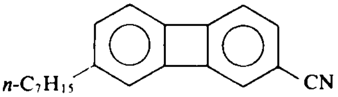
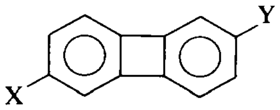
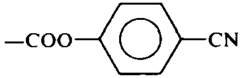
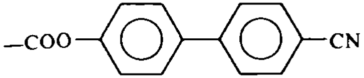
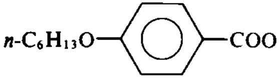
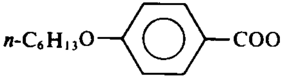
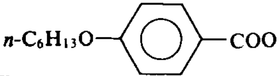
	mp (°C)	CP (°C)
	44.5	55
	28	42
	132–4	
	121	

TABLE VI

Effects of the aromatic system



X	Y	mp (°C)	CP (°C)
n-$C_6H_{13}O$ *n*-$C_6H_{13}CO$	*n*-$C_6H_{13}O$ *n*-$C_6H_{13}CO$	118–9 171–2	
n-C_7H_{15}		118	(104–75)
n-C_7H_{15}		164	217(S—N)266
		154	272
	C_2H_5O	136	170

From the above mentioned observations, it might be proper to emphasize here again that even various structural features can generally be divided into favorable, less favorable and unfavorable categories; it is only the net result of the combination and counterbalance of the functions of the molecular substructures that count in determining whether a compound with given structural features will be mesogenic or not.

2 Molecular structures and monotropic mesomorphism

In all the monotropic mesogens, the melting points are always equal to or higher than the clearing points, and the compounds must show supercooling properties. Therefore, structural features which would lead to the enhancement of the crystal lattice and weakening of the mesogenic order are expected to give formation of monotropic mesophases.

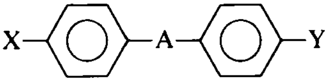
The substitution of an α-hydrogen atom by a methyl group in a terminal chain of an enantiotropic azomethine is often enough to bring about the monotropic phenomenon, but in the same type of enantiotropic compound with a more extended conjugated system, a larger ethyl side chain instead of a methyl group is required in the terminal chain to show the same effect (Table VII).

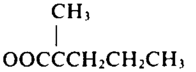
The nature of the terminal groups also appears very important; for instance,

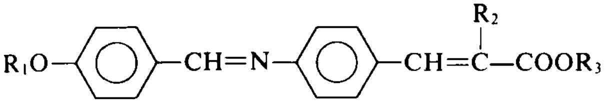
TABLE VII

Factors leading to monotropic mesophases

Chain branching



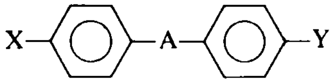
X	A	Y	mp (°C)	CP (°C)
n-C_4H_9O	—CH=N—	$OOCCH_2CH_2CH_2CH_3$	43	70
n-C_4H_9O	—CH=N—	 $OOC\overset{CH_3}{\overset{\vert}{C}}CH_2CH_2CH_3$	63	(53)[12]



R₁	R₂	R₃	mp (°C)	CP (°C)
C_2H_5	CH_3	*n*-C_3H_7	88	117
C_2H_5	C_2H_5	*n*-C_3H_7	96	(64-34)
n-C_4H_9	CH_3	*n*-C_3H_7	102	110
n-C_4H_9	C_2H_5	*n*-C_3H_7	73	(54-40)

TABLE VIII

Effects of the nature of terminal groups



X	A	Y	mp (°C)	CP (°C)	Ref
C_2H_5O	—CH=N—	n-C_2H_9	36	80	8
CH_3COO	—CH=N—	n-C_4H_9	55	(50–43)	6

the replacement of an alkoxy by a corresponding acyl group in enantiotropic azomethines usually results in monotropic mesomorphism (Table VIII), but the reason is not clear.

It is interesting to note that the mutual exchange of the terminal groups in enantiotropic mesogens with unsymmetrical bridging linkages often gives a monotropic mesogen, and *vice versa* (Table IX).

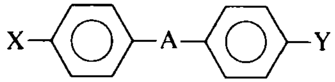
For certain ester type mesogens, the exchange of terminal groups seems able to afford an isomeric molecule with a higher polarity which would be expected to give enhancement of lateral interactions of a polar nature, and hence might lead to a higher melting point rather than a higher clearing point (Table X).[7]

Sometimes one can even see a delicate change from an enantiotropic to a monotropic mesophase when the length of the terminal *n*-alkyl group undergoes a change of only one carbon atom (Table XI).

Finally, it is observed that while the methoxy/*n*-butyl terminal combination in azomethine, azo, and azoxy compounds always gives enantiotropic mesogens, the corresponding ester compound turns out to be monotropic. This might be attributed to free rotation about the C—O single bond which

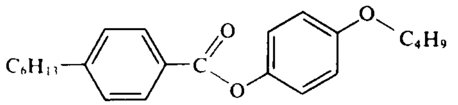
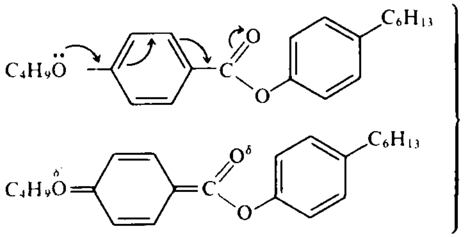
TABLE IX

Effects of exchange of terminal groups



X	A	Y	mp (°C)	CP (°C)	Ref
CH_3O	—CH=N—	n-C_4H_9	21	47	8
n-C_4H_9	—CH=N—	OCH_3	48	(39)	13
n-C_6H_{13}	—COO—	$OC_4H_9(n)$	39	49	7
n-C_4H_9O	—COO—	n-C_6H_{13}	67	(54)	7

TABLE X

	mp (°C)	CP (°C)
	39	49
	67	(54)

would lead to a conformation change, which in turn might result in a reduction of the polarizability anisotropy and geometric anisotropy of the molecule (Table XII).

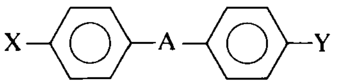
3 The design of low-melting mesogens with broad nematic range

The fast development in the use of liquid crystal materials in the display industry in the past decade has enormously stimulated the design and synthesis of mesogens with low melting points and broad nematic range. This goal can usually be achieved by depression of the melting points and simultaneous raising of the clearing points of the mesogens through molecular design.

The incorporation of unsymmetrical substitution in mesogenic compounds with 3 benzene rings usually gives a marked effect on melting point depression as shown in Table XIII, and the replacement of terminal alkoxy or acyloxy

TABLE XI

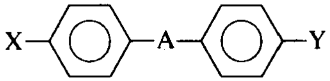
Effects of length of terminal *n*-alkyl groups

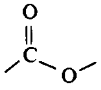
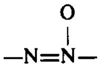
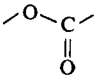


X	A	Y	mp (°C)	CP (°C)	Ref
CH_3O	—CH=N—	*n*-C_4H_9	21	47	8
CH_3O	—CH=N—	*n*-C_3H_7	45	60	14
CH_3O	—CH=N—	C_2H_5	57	(28)	8
CH_3O	—CH=N—	CH_3	92	(38)	8

TABLE XII

Rigidity and linearity of the bridge linkage

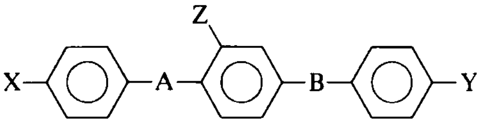


X	A	Y	mp (°C)	CP (°C)	Ref
CH$_3$O	$-N=N-$	n-C$_4$H$_9$	32	49	8
CH$_3$O	 $-\overset{\overset{O}{\|}}{C}-O-$	n-C$_4$H$_9$	40	(24)	—
CH$_3$O	 $-N=\overset{\overset{O}{\mid}}{N}-$	n-C$_4$H$_9$	41	74	—
CH$_3$O	 $-O-\underset{\underset{O}{\|}}{C}-$	n-C$_4$H$_9$	63	(22)	15

groups by a n-alkyl group of medium size (e.g., C$_4$—C$_7$) usually tends to lower the melting point also (Table XIV).

As for how to effect an increase in the clearing point or an enhancement of the thermal stability of the mesophases, it must be borne in mind that the optimum combination of terminal groups and bridging groups is most important.

TABLE XIII

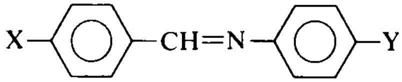


X	A	Z	B	Y	mp (°C)	CP (°C)
sym. C$_2$H$_5$O	COO	H	OOC	OC$_2$H$_5$	226	287
unsym. CH$_3$O	COO	H	OOC	OC$_3$H$_7$	167	277

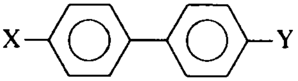
X	A	Z	B	Y	mp (°C)	CP (°C)
sym. n-C$_5$H$_{11}$	OOC	Cl	COO	n-C$_5$H$_{11}$	86	119.5
unsym. n-C$_5$H$_{11}$	OOC	Cl	OOC	n-C$_5$H$_{11}$	39	122

TABLE XIV

Presence of terminal *n*-alkyl group and m. p. depression



X	Y	mp (°C)	CP (°C)	Ref
CH_3O	$OOCC_2H_5$	70	114	7, 16
CH_3O	*n*-C_4H_9	21	47	8



X	Y	mp (°C)	CP (°C)	Ref
n-$C_5H_{11}O$	CN	48	67.7	17
n-C_5H_{11}	CN	22.5	35	17

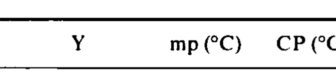
Owing to the presence of a terminal CH_3O group, the replacement of the $OOCCH_3$ group in APAPA by a butyroyloxy group lowers the melting point by as much as 31°, while having little effect on the clearing point, thus resulting in a nematic range broadening of 32° (Table XV).

The presence of a terminal ethoxy group has proved especially effective in raising the clearing point, although both the methoxy and the ethoxy groups are known to be favorable in enhancing the thermal stability of mesophases. Thus, EBBA has a clearing point much higher than MBBA, and the nematic range is broadened considerably (Table XVI).

Sometimes however we have to use both methods to effect the broadening of the nematic range; for instance, we can depress the melting point through terminal chain branching and simultaneously raise the clearing point by optimum compatibility of the terminal groups. The formation of a low-melting

TABLE XV

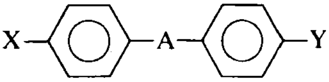
Optimum compatibility of terminal groups



X	A	Y	mp (°C)	CP (°C)	N.Range (°C)	Ref
CH_3O	—CH=N—	$OOCCH_3$	81	108	27	16
CH_3O	—CH=N—	$OOCC_3H_7$-*n*	50	109	59	16

TABLE XVI

Elevation of T_{NI} by optimum compatibility of terminal groups



X	A	Y	mp (°C)	CP (°C)	N.Range (°C)	Ref
CH_3O	—CH=N—	n-C_4H_9	21	47	26	8
C_2H_5O	—CH=N—	n-C_4H_9	32	80	48	8

and broader range chiral nematic (as shown in Table XVII) offers a good example.

As a final example of molecular design, the insertion of an ester linkage into a well known terphenyl mesogen has also led to simultaneous melting point lowering and clearing point raising; as a result, a lower-melting mesogenic ester with a broader nematic range was obtained (Table XVIII).

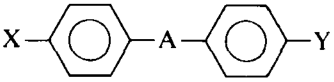
CONCLUSION

It is the viewpoint of the author that, although the quantitative approach to the calculation of the transition temperatures for thermotropic liquid crystal materials is developing rapidly, further accumulation of experimental facts leading to qualitative predictions of the trends in phase transition behavior is still essential for the molecular design of nematic liquid crystal materials with the desired thermal properties; at least this is the situation for the time being and from a practical point of view.

TABLE XVII

Typical examples of molecular design of low melting—broad range NLC

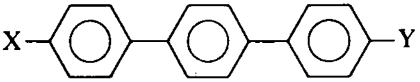
1. Depression of mp. *via* chain branching
2. Increase in T_{NI} by end group compatibility



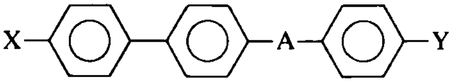
X	A	Y	mp (°C)	CP (°C)	N.Range (°C)	Ref
CH_3O	—CH=N—	$CH_2CH_2CH_2CH_3$	21	47	26	8
C_2H_5O	—CH=N—	$CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}H}CH_2CH_3$	15	60	45	18

TABLE XVIII

Incorporation of a flexible bridge linkage into terphenyls



X	Y	mp (°C)	CP (°C)	N.Range (°C)	Ref
CN	n-C_7H_{15}	134	222	88	17



X	A	Y	mp (°C)	CP (°C)	N.Range (°C)	Ref
CN	OOC	n-C_7H_{15}	92	224	132	7

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