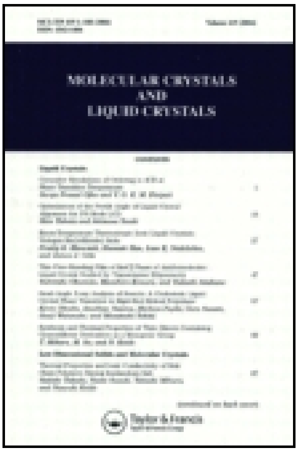

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Behavior of Novel Dimesogenic Compounds

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To cite this article: Jung-Il Jin (1995): Liquid Crystalline Behavior of Novel Dimesogenic Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 249-265

To link to this article: http://dx.doi.org/10.1080/10587259508034002

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 249–265
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LIQUID CRYSTALLINE BEHAVIOR OF NOVEL DIMESOGENIC COMPOUNDS

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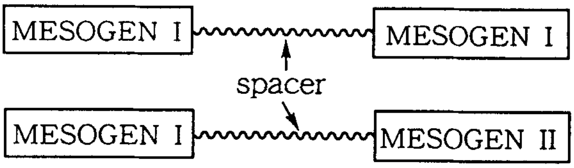
Abstract Liquid crystalline behavior of many series of novel dimesogenic compounds having two identical or two different mesogenic units attached to both ends of a central flexible spacer is reviewed in this article. When central spacers are polymethylene units, these compounds reveal a strong odd-even effect not only in melting point (T_m) and isotropization temperature (T_i), but also in entropy (ΔS_i) of isotropization. Variety of mesophases that are formed by dimesogenic compounds having two identical mesogenic units is much less than that shown by the corresponding monomesogenic compounds. The nematic and smectic group efficiency of terminal substituents in dimesogenic liquid crystals is similar as in monomesogenic compounds. It is also learned that mesomorphic behavior of dimesogenic compounds carrying two different mesogenic units is not a simple combination of those of each mesogenic elements. Some of such dimesogenic compounds reveal unexpected, extraordinary thermal transition sequences which have never been observed to occur in the common monomesogenic compounds, and the incommensurate S_A and twisted grain boundary (TGB) phases are formed.

INTRODUCTION

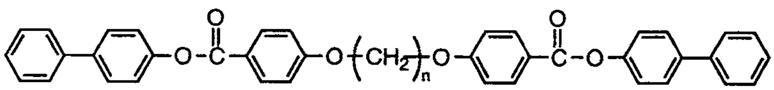
Liquid crystalline behavior of dimesogenic compounds opens a new area of research in liquid crystals science. The term 'dimesogenic compounds' describes thermotropic compounds consisting of two mesogenic units linked through a central spacer such as polymethylene and oligosiloxyl groups. The two mesogenic units may or may not be identical. When they are identical, they are occasionally called twin or siamese compounds.



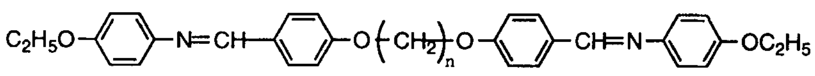
This type of compounds are important not only as a new class of liquid crystalline compositions but also as models for the corresponding main chain liquid crystalline polymers containing flexible spacers. In this report we would like review the structure-property relationship of dimesogenic compounds by analyzing mainly their phase behavior. Most of the compounds dealt with deeply in this article have been prepared and reported earlier by us. The structural variables to be discussed are 1) length of central spacers, 2) structure of spacers, 3) nature of terminal substituents, 4) compounds having two different mesogens and 5) mutual miscibility.

LENGTH OF CENTRAL POLYMETHYLENE SPACERS

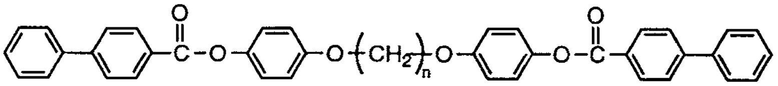
It has been repeatedly observed that transition temperatures, i.e., T_m and T_i, of thermotropic main chain polymers reveal so-called the odd-even dependence on the number of the methylene units in the flexible spacers.[1-4] A similar phenomenon could even more definitely be observed for a series of twin dimesogenic compounds consisting of central polymethylene spacers and a variety of mesogenic units.[5-8] Some of the representative examples are given below :



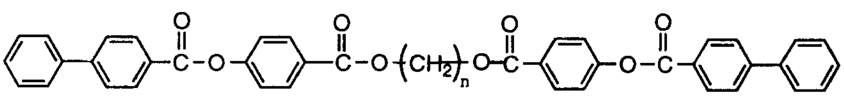
Series I (n = 4-10)[5]



Series II (n = 2-10)[6]



Series III (n = 2-10)[7]



Series IV (n = 2-10)[8]

All of these series of compounds exhibit a more or less the same odd-even dependence of T_m, T_i, ΔH_m, ΔH_i and ΔS_i values on the number of the methylene units in the central spacer.

Figure 1 and 2 show the dependence of T_m and T_i values of series I [5] and of

ΔS_i values of series II^6 on the length of the spacers, respectively. Figure 1 clearly demonstrates that the T_m and T_i values of the compounds having even number of the methylene units in the spacer are consistently higher than those of odd number of the methylene units. And, in general, the T_m and T_i values of the dimesogenic compounds are much higher than those of the corresponding monomesogenic compounds. The mesophase temperature range, i.e., T_i-T_m, however, seems to diminish for the dimesogenic compounds when compared with the corresponding monomesogenic counterparts, which indicates that the presence of two rigid cores in the formers raise T_m values greater than T_i values. In addition, it is rather surprising to see in Figure 2 that the entropy of isotropization also reveals similar alternation behavior and also that the values for even members are significantly greater than those for odd series

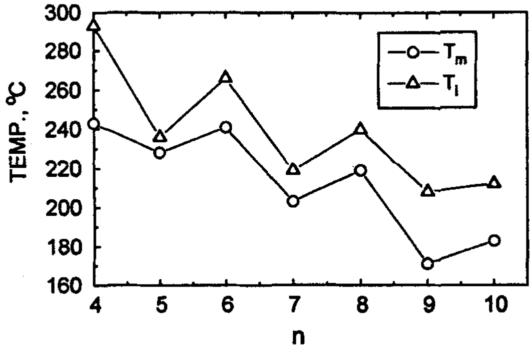


FIGURE 1 Dependence of T_m and T_i of compounds I on the length, n, of polymethylene spacer.

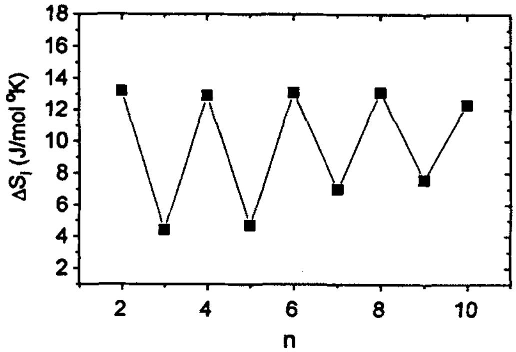


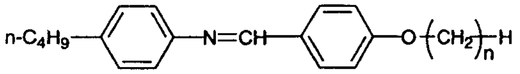
FIGURE 2 Dependence of ΔS_i of compounds of II on the length, n, of polymethylene spacer.

indicating a higher orientational order in the even compounds than in the odd ones. One, however, has to pay one's attention to the fact that the degree of alternation in the magnitude of T_i and ΔS_i gradually decreases as the length of the spacer increases. This can be ascribed to the increased degree of rotational, conformational freedom along the carbon-carbon single bond with increased number of the methylene units in the spacer. There are some theoretical as well as experimental evidence[9-11] that the polymethylene spacers tend to have a trans zig-zag conformation when the length of a spacer is not too long in main chain thermotropic polymers. But it is conceivable that conformational irregularity of polymethylene spacers increases as the length of a spacer increases regardless whether it be a part of a dimesogenic compound or a polymer. This will lead to a reduced difference in mesophase-isotropic transitional properties for longer spacers between odd and even members.

Luckhurst and coworkers[12-14] proposed a successful molecular field theory to explain the odd-even effect based on a simple model that the methylene groups in a spacer of a dimesogenic compound is consisting of linear and bent conformations. They compared their theoretical predictions with the experimental results for α,ω-bis(4,4'-cyanobiphenyloxy)alkanes.[15] According to their model, orientational contribution to the odd-even effect appears to be greater than conformational contribution.

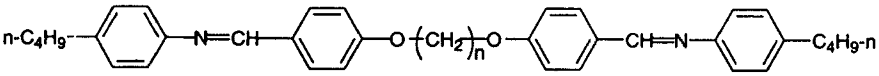
Another important point to be noted is the fact that the heat of isotropization, ΔH_i, of dimesogenic compounds ranges from 5 to 15 % of the heat of melting, ΔH_m.[5-8,16] This is much higher than the usual value of about 1-3 % for the monomesogenic compounds.[17] It appears that two mesogenic units present in a same molecule tend to increase the value of ΔH_i much greater than the value of ΔH_m. The absolute values of ΔH_m and ΔH_i of dimesogenic compounds are, as expected, much greater than those of monomesogenic liquid crystals.[5-8,17] Especially, ΔH_i values of dimesogenic liquid crystals are very frequently several times the ΔH_i values of monomesogenics. The same is true for ΔS_i values, as thermodynamics would predict. For example, the ΔH_m values of the series I compounds range from about 40 KJ/mole to 70 KJ/mole, while those of ΔH_i range from 3.8 KJ/mole to 7.3 KJ/mole.[5] The ΔS_i values lie in the range of 7.5-16 J/mol K.[5]

As the nature of mesophases is concerned, the variety of mesophases formed by dimesogenic compounds is less than that observed for the corresponding mono-mesogenic liquid crystals. For example, 4-n-butyl-N-[4-n-alkoxybenzylidene]anilines form only nematic phase when the alkoxy group is methoxy, ethoxy or propoxy group. Longer alkoxy groups tend to favor the formation of more than one smectic phases before reaching nematic state. n-Pentoxy and n-hexyloxy compounds, however, reveal a wide variety of mesophases as exhibited often by Schiff-base type liquid crystals.



n = 5 ; K 24 S_B 52 S_A 54 N 71 I[18]
n = 6 ; K 35 S_B 59 S_C 60 S_A 69.5 N 77.7 I[16,18]
n = 10; K 40 S_x 68 S_y 73 S_A 85 I[19]

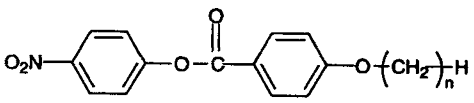
Such a phase behavior is in a great contrast to the phase behavior of the following dimesogenic compounds.[16]



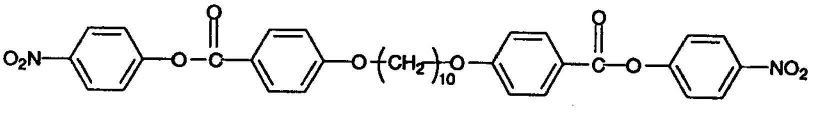
n = 2 ; K 205 S_A 237 I
n = 4 ; K 146 S_C 151 S_A 213 I
n = 5 ; K 116 N 127 I
(K 88 S_A 112 N 124 I on cooling)
n = 10 ; K 134 N 148 I

First of all, none of the dimesogenic compounds forms the S_B phase. Moreover, the shorter the central spacer, the higher is the tendency to form smectic phases. This trend is completely reversed when compared with monomesogenic compounds. This type of reversal in phase transition behavior, however, is not universal. Date et al.[20] recently reported liquid crystalline behavior of similar compounds having a much wider variety in the length of spacers and also in the length of the two teminal tails. They found that increasing the spacer length for a given terminal tail favors the formation of nematic phases, as observed for the above series by us, while increasing the tail length for a given spacer promotes the formation of smectic phases. They also observed the occurrence of smectic F-smectic A and crystal G-isotropic transitions as well as novel modulated hexatic phases for some of the compounds. The series IV compounds[8] form only nematic phase when the central spacer is short (n = 2 or 3), and the nematic and smectic phases when the length of the spacers is medium, i.e., n = 4-7. And longer spacers induce the formation of a smectic phase only. This is completely in line with the phase behavior of the corresponding monomesogenic series.

Another interesting comparison between the phase behavior of monomesogenic and dimesogenic compounds can be found in phase transitions of the following compounds.



n = 5 ; K 62 I (monotropically N 54 I)[21]
n = 10; K 55 S_A 77.5 I[21]

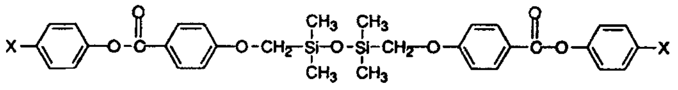


K 144 N 160 I[5]

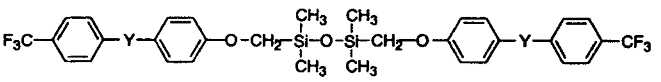
The monomeric compound with n = 5 forms the nematic phase only monotropically, but its dimer forms the nematic phase enantiotropically. This can be taken as an indication that dimeric compounds have a greater tendency to be thermotropic. But, the examples available are still rather limited, and it is clear that further studies are necessary before one can put forward a firm conclusion on this respect.

STRUCTURE OF SPACERS

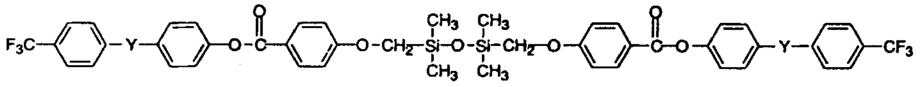
The structure of the central spacer influences profoundly not only the thermodynamics of transitions but also the nature of mesophases formed. The representative examples can be found in the following three series of compounds.



Series V (X = H, CH_3, OCH_3, Cl, CN, NO_2 and C_6H_5)[22]

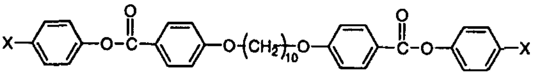


Series VI (Y = $-O-\overset{O}{\overset{\|}{C}}-$, $-NH-\overset{O}{\overset{\|}{C}}-$, $-\overset{O}{\overset{\|}{C}}-O-$)[23]



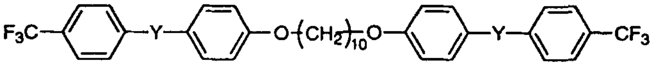
Series VII (Y = $-O-\overset{O}{\overset{\|}{C}}-$, $-NH-\overset{O}{\overset{\|}{C}}-$, $-\overset{O}{\overset{\|}{C}}-O-$)[23]

Surprisingly, all of the series V[22] formed smectic phases regardless of the nature of the terminal substituent. This is in a direct contrast to the fact that all of the following series form only nematic phases.[5]



Series VIII (Y = H, CH_3, CH=O, Cl, CN, NO_2 and C_6H_5)[5]

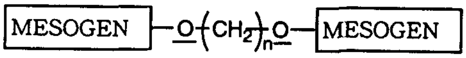
Moreover, transition temperatures of V compounds[22] were much lower than those of the corresponding VIII compounds[5]; for example, the T_m and T_i values of V-H (compound V with X = H) are 52° and 75 ℃, respectively, whereas the values for VIII-H are 121.5 and 127.5 ℃, respectively. Another interesting point to be noted is the fact that ΔH_m values of the disiloxyl compounds are extremely low when compared with those of the polymethylene compounds. The ΔH_m values of series V range from about 14 to 45 J/g, while those of series VIII are in the order of 100 J/g. The values of ΔH_i, however, are comparable. The relatively low values of ΔH_m for series V are probably due to the large size of substituent in the spacer and very low rotational energy barrier of the disiloxyl spacer. Easy conformational adjustment, however, will centainly allow the mesogenic units to form smectic layers. The same explanations can be given to the observation that the series VI compounds[23] form S_A phases monotropically, while the corresponding compounds containing the decamethylene spacer are not thermotropic.[23]



nonmesomorphic

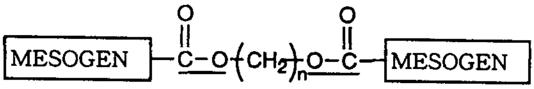
All of the series VII compounds[23] are enantiotropically liquid crystalline and form the S_A phase. Certainly, the longer mesogenic units enhance mesophase-forming ability of a compound; the monotropic compounds of series VI contain diad aromatic ester or amide or esteramide as mesogens whereas series VII contain triad mesogens and are enantiotropic. These compounds, especially of series VII, also exhibit relatively low heats of melting (ΔH_m~40-70 J/g). The spacer in series VI and VII seems to reduce the crystal lattice energy and intermolecular interactions in the solid state again due to its flexibility and also bulkiness. The examples given, although limited, clearly demonstrate how strongly the spacers control not only the thermodynamics of phase transitions but also the nature of mesophases formed by the dimesogenic compounds under discussion.

Comparison of the phase behavior of the series IV compounds[8] with the behavior of the series III compounds[7] reveals a very interesting point. The latters form nematic phase enantiotropically as explained earlier. The nature of the mesophases formed by the formers, however, strongly depends on the length of the spacer. The only structural difference between the two series lies in the structure of linking group between the mesogenic unit and the central polymethylene spacer; ether linkage in series III vs. carboxy linkage in series IV.



$\boxed{\text{MESOGEN}}-O\!\left(CH_2\right)_n\!O-\boxed{\text{MESOGEN}}$

(Series III)

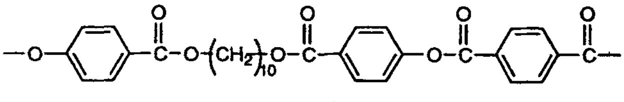


$\boxed{\text{MESOGEN}}-\overset{O}{\overset{\|}{C}}-O\!\left(CH_2\right)_n\!O-\overset{O}{\overset{\|}{C}}-\boxed{\text{MESOGEN}}$

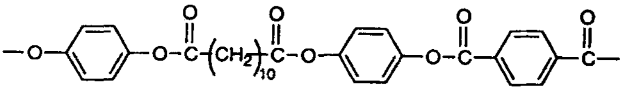
(Series IV)

For series IV, the compounds with n = 2, 3, 7, 9 and 10 are monotropic and those with 4, 5 and 6 are enantiotropic. And the compounds with n = 2 and 3 form nematic phase, while those with n = 4-7 form nematic as well as smectic phases. The compounds with longer spacers (n = 8-10) show only a smectic phase. The presence of carbonyl group attached to the mesogens certainly increases lateral interaction due to its influence on dipole direction and the magnitude of the permanent dipole moment. A slight increase in the length of the hard core by the carbonyl group and longer spacers favor the formation of smectic phase as in monomesogenic series.

A fact relative to this observation is the completely different phase behavior of the following two polymers.[24]



K 193 S 216 I



K 215 N 287 I

The former forms a smectic phase, whereas the latter forms a nematic phase. Here again, the difference between the two polymers is only in the structure of the linking groups between the mesogens and spacers, i.e., $-\overset{O}{\overset{\|}{C}}-O-$ vs. $-O-\overset{O}{\overset{\|}{C}}-$.

TERMINAL GROUPS ON MESOGENIC UNITS

There have been many reports discussing[25-28] about the electronic as well as steric effects of the terminal groups (X and Y in the molecular structure shown below) on the thermotropic behavior of monomesogenic compounds.

$$X-\boxed{\text{HARD CORE}}-Y$$

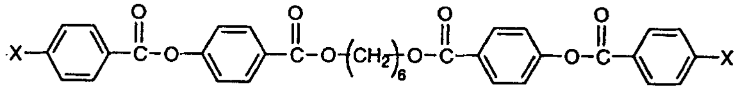
Scientists generally have been paying their attention to how X or Y or both would influence the transition temperatures and the nature of mesophases formed. And it has been rather well established that a substituent can change the breadth and also the magnitude and direction of the permanent dipole moment of a molecule, both of which control the thermal stability or mesophase temperature range and nature of mesophases formed by a compound.

Although there are minor exceptions depending on the structure of the central hard core, it appears that the N-I transition temperature is influenced mainly by the change in molecular diameter caused by the size of a substituent : the N-I transition temperature drops down rapidly as molecular diameter increases.[25] On the contray, the S-N and S-I transition temperatures appear to be influenced more by electronic effect, i.e., change in dipole moment (magnitude and direction) by a substituent.[25]

In addition to series V and **VII**, we have prepared many different series of dimesogenic compounds carrying various terminal substituents, in order to see if substituent effects in those compounds are the same or not as in monomesogenic compounds. All of the compounds of series **VIII**[5] formed only the nematic phase enantiotropically and their N-I transition temperatures are 127.5, 146, 156, 160, 162.5, 181 and 212 ℃, respectively, in the order of substituents listed in the above parenthesis.[5,29] The melting temperatures of the compounds also increased more or less in a parallel fashion. Judging from the clearing temperatures (T_i) of this series, the ability of a substituent to stabilize the nematic phase increases in the following order :

$$H < CH_3 < Cl < NO_2 \approx CH{=}O < CN < C_6H_5$$

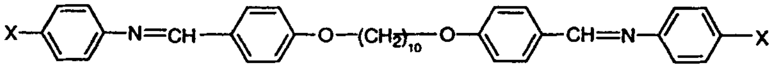
This order is very silimar to that found for monomesogenic compounds.[26-28] We[8] have observed a similar nematic group efficiency order ($CH_3 < NO_2 < CH_3O < C_6H_5$) for the following compounds.



Series IX (X = CH_3, NO_2, CH_3O and C_6H_5)[8]

The compounds with X = CH_3, NO_2 and CH_3O are monotropic and the one with X = C_6H_5 is enantiotropic.

The following Schiff-base type compounds (series X) reveal an interesting phase behavior:[6]



Series X (X = H, CH_3, NO_2, OCH_3, CN, $COOCH_3$ and C_6H_5)[6]

The series X with X = H is not liquid crystalline and the rest are thermotropic. The compounds with X = CH_3 or OCH_3, however, are only monotropic while others are enantiotropically thermotropic. Thermotropic compositions all form nematic phases. Transition temperatures are X = CH_3, K 141 N 161 I ; NO_2, K 149 N 179 I ; OCH_3, K 167 N 189 I ; CN, K 151 N 200 I ; $OCOCH_3$, K 161 N 201 I ; OC_2H_5, K 190 N 202 I. Therefore, even for the series X, the nematic group efficiency similar for ester type compounds is observed.

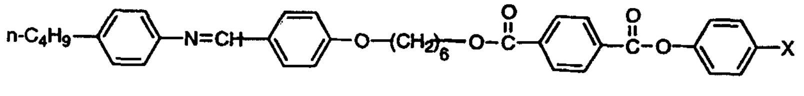
$$H < CH_3 < NO_2 < OCH_3 < CN \approx OCOCH_3 \approx OC_2H_5$$

As mentioned earlier, the series V compounds[22] form smectic phases in melts, and the S-I transition temperature increases in the order of X = H (75 ℃) < CH_3 (114 ℃) < Cl (118 ℃) = NO_2 (118 ℃) < CN (124 ℃) < OCH_3 (128 ℃) < C_6H_5 (158 ℃). This order is, again, in good agreement with those found in many series of monomeric smectic compounds.[26,28]

In light of the observations made on the several examples given, it can be said that the ability of a terminal substituent to stabilize mesophases formed by dimesogenic compounds is basically the same as in monomesogenic compounds; either enhanced polarizability or increased polarity or lengthening of the rigid rod-like structure by the substituent or a combination thereof appears to be the most important factors in stabilization of the nematic phase. Increase in lateral interaction by a substituent tends to favor the formation of a smectic phase.

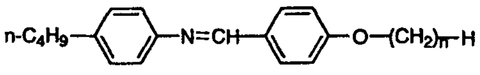
LIQUID CRYSTALS HAVING TWO DIFFERENT MESOGENIC UNITS

Our discussion up to this point was concentrated to the liquid crystalline behavior of dimesogenic compounds carrying two identical mesogenic units. Recently, we became interested in the liquid crystalline properties of the dimesogenic compounds consisting of two chemically different mesogenic rigid units and a central spacer. The first series of compounds studied are shown below :[30]

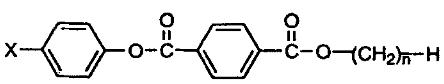


Series XI (X = H, Cl, CN, NO_2, n-C_4H_9 and C_6H_5)[30]

The monomeric structures of these compounds reveal the following phase behavior :



n = 3 ; K 41.1 N 55.7 I (S_A 23.3 monotropic)[18]
n = 6 ; K 35 S_B 59 S_C 60 S_A 69.5 N 77.7 I[30]



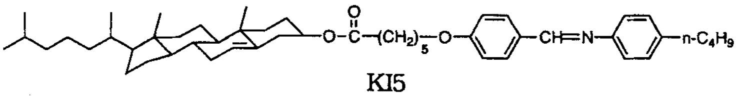
X = H, Cl, CN, NO_2, n-C_4H_9 and C_6H_5
n = 3 and 6 ; non-liquid crystalline[30]

The compounds of series XI with X = H, Cl and CN are found to be non-mesomorphic. On the contrary, those with X = NO_2, n-C_4H_9O, and C_6H_5 are mesomorphic :[30]

X = NO_2 ; K 145 N 190 I (K 128 S_A 163 N 183 I on cooling)
X = n-C_4H_9O ; K 128 S_A 165 N 175 I
X = C_6H_5 ; K 169 S_A 190 N 216 I

Certainly, one cannot find any parallelism between the mesophases formed by the dimesogenic compounds and those formed by each monomesogenic elements. In other words, liquid crystalline behavior of dimesogenic compounds having two different rigid units is not a simple combination of those of each monomeric components.

The phase transition sequence of the following compound is even more perplexing.[31]



KI5

The compound KI5 exhibits a completely new thermal transition sequence, which has never been observed before, including incommensurate S_A (S_A^{inc}) and chiral S_C phases appearing twice :[31]

$$\text{Crystal} \xrightarrow{85\ ^\circ\text{C}} S_A^{inc} \xrightleftharpoons{144.5\ ^\circ\text{C}} S_C^{*} \xrightleftharpoons{149\ ^\circ\text{C}} S_A^{inc} \xrightleftharpoons{151.5\ ^\circ\text{C}} S_C^{*} \xrightleftharpoons{165\ ^\circ\text{C}}$$

$$\text{TGB} \xrightleftharpoons{168\ ^\circ\text{C}} N^{*} \xrightleftharpoons{192\ ^\circ\text{C}} \text{I}$$

The differential scanning calorimetry, X-ray diffraction measurements and optical microscopic studies support the above phase sequence.

For the S_A^{inc} phases,[32-34] small angle X-ray diffractions show a weaker peak corresponding to the spacing of 36 Å which cannot be directly related to any molecular parameter in addition to two stronger diffractions at the spacing of about 44 and 20 Å. The first one is very close to total molecular length of 46 Å in the most extended conformation (Figure 3) and the second probably to the length of cholesteryl (20 Å) or Schiff-base (18 Å) moiety. We still do not understand exactly how the formation of incommensurate phaseses depend on molecular parameters, and need to conduct much further studies. Nevertheless, it is clear that studies on the phase behavior of dimesogenic and also multimesogenic compounds consisting of mesogenic units of chemically different structures can provide us with further insight into this important phenomenon. Recently Attard et al.[35] reported the liquid crystalline properties of the following non-symmetric dimeric compounds. They found an interesting fact that some of the compounds form the intercalated or interdigitated smectic A phase depending on the values of m and n.

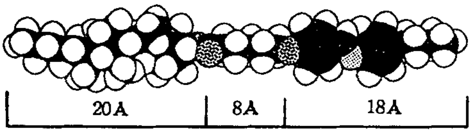
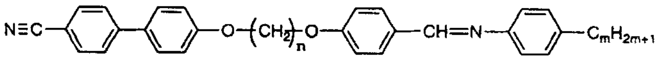


FIGURE 3 Molecular shape of KI5.



MISCIBILITY OF DIMESOGENIC COMPOUNDS

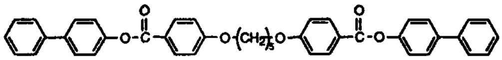
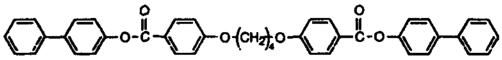
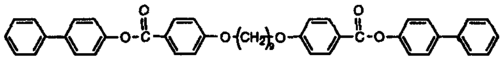
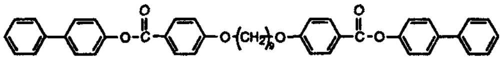
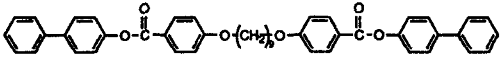
Mutual miscibility between dimesogenic nematic compounds was studied earlier by us[36] using a series of compounds. And it was found that nematic dimesogenic compounds (Table I) having a wide variety of structures are miscible in mesophases with each other over the whole range of compositions and that the Schröder-van Laar equation correctly predicts, within experimental error, the melting temperatures and compositions of eutectic mixtures (Table II).

$$-\ln x_1 = \frac{\Delta H_m{}^1}{R}\{(1/T) - (1/T_m{}^2)\}$$

$$-\ln x_2 = -\ln(1-x_1) = \frac{\Delta H_m{}^2}{R}\{(1/T) - (1/T_m{}^2)\}$$

where ΔH_m's are heats of melting and x's are mole fractions of compound 1. The numbers 1 and 2 stand for each component.

Table I Structure of dimesogenic compounds.

Compounds 1	
E - 5	
E - 4	
E - 9	
E - 9	
E - 9	

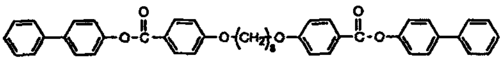
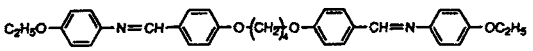
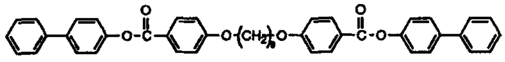
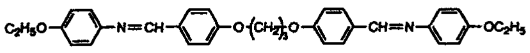
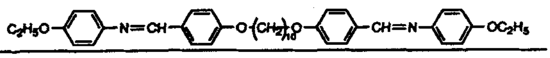
Compounds 2	
E - 8	
P - 4	
Y - 9	
P - 3	
P - 10	

Table II Eutectic compositions and eutectic melting points

						Experimental		Calculated	
Compound 1	Compound 2	T_m^1 K	ΔH_m^1 KJ/mole	T_m^2 K	ΔH_m^2 KJ/mole	T_{eu} K	X_{eu} mole%	T_{eu} K	X_{eu} mole%
E-5	E-8	496	42.8	488	51.2	475	0.48	465	0.48
E-4	P-4	515	68.2	489	44.4	480	0.27	476	0.27
E-9	Y-9	442	37.2	429	20.2	--	--	414	0.19
E-9	P-3	442	37.2	448	38.2	427	0.61	426	0.61
E-9	P-10	442	37.2	463	67.4	438	0.80	436	0.86

Figure 4 and 5 show phase diagrams for the E-9/P-3 and E-9/P-10 pairs. The compositions forming eutectic mixtures all revealed five regions (I - V) in the phase diagrams: (I) solid 1 plus solid 2, (II) solid 1 plus nematic phase, (III) solid 2 plus nematic phase, (IV) nematic phase, and (V) isotropic phase. The E-9/Y-9 pair was unique in that melting point of the mixture changed continuosly over the whole range of composition. This is a strong indication that cocrystallization occurs during cooling process. Eutectic formation could not be observed for this pair. As a result, only three regions (I-III) exist in the phase diagram (Figure 6): (I) solid 1 plus solid 2, (II) nematic phase, and (III) isotropic phase.

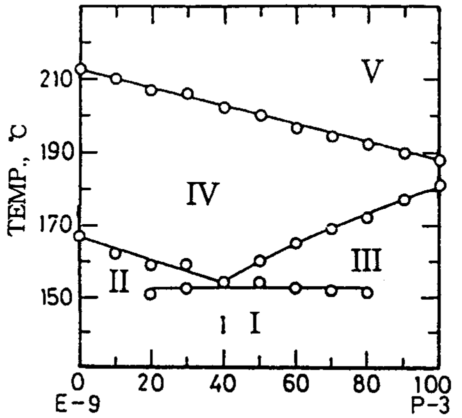


FIGURE 4 Phase diagram for P-3 and E-9 mixtures.

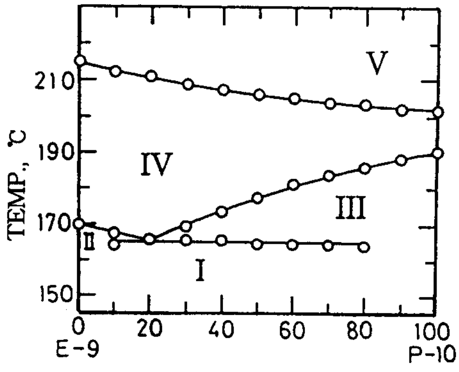


FIGURE 5 Phase diagram for P-10 and E-9 mixtures.

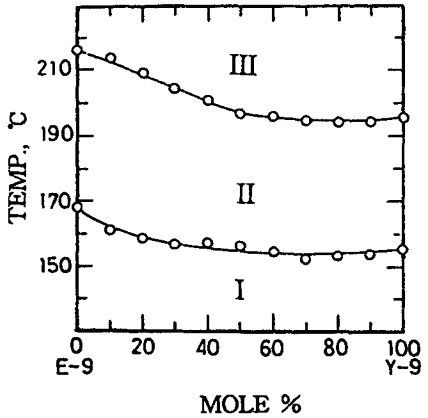


FIGURE 6 Phase diagram for Y-3 and E-9 mixtures.

We also have found that dimesogenic nematic compounds are miscible with nematic or cholesteric main chain polyesters containing flexible spacers.[37] The Schröder-van Laar equation does not seem to be applicable to the mixtures of liquid crystalline polymers and dimesogenic compounds, although eutectic compositions and melting temperatures of mixtures are not too far from those theoretically predicted only when the structures of the repeating units of polymers and dimesogenic compounds are similar.

CONCLUSION

Dimesogenic compounds consisting of two mesogenic units interconnected through a central spacer are particularly interesting class of thermotropic compound : they are new liquid crystals per se whose structure-property relationships have yet to be established.

Nevertheless, we have tried to review the structure-property relationship of dimesogenic compounds in a systematic way by analyzing the observations made mainly in our laboratory. Although the data available are still limited, it is obvious that this class of compounds opens a new chapter in liquid crystals sciences and enable us to design the structures of new liquid crystals with a wide variety of properties. Expansion of such studies even further to tri-[38-40] and multimesogenic compounds is expected to result in many new exciting discoveries. Especially, phase behavior of di- and multimesogenic compounds carrying chemically different mesogenic units will require a lot of structural analyses and theoretical investigations.

ACKNOWLEDGMENT : We are grateful to the Ministry of Education, Republic of Korea, for the support of this research (BSRI-94-3406) in the fiscal year of 1994 through the Research Institute of Basic Sciences, Korea University.

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