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Research Article

Effect of Molecular Structure on the Phase Behavior of Ternary Mixtures Made from Unsymmetrical 1,4-Phenylene bis 4-Substituted Benzoates

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Ternary mixtures formed from components of the five series of unsymmetrical 1,4-phenylene bis-4-substituted benzoates (**In**$_{a–e}$), in which the substituent (X) alternatively changed from CH_3O, CH_3, Cl, NO_2, and CN, respectively, while, within each homologous series, the length of the terminal alkoxy group varies between $n = 6$, 8, or 14 carbons, were prepared and characterized for their mesophase behaviour. Transition temperatures of the mixtures prepared were measured by differential scanning calorimetry and the phases identified by polarized-light microscopy.

1. Introduction

In order to be used as electronic displays or in any other electro-optical application, liquid crystalline materials should exist in a mesomorphic phase at ambient temperatures. As is true for other solids, the melting point of a liquid crystalline compound is depressed by the addition of another substance, and a mixed mesophase results in which the mesomorphic range begins at a lower temperature. If the added substance is structurally similar to the host compound, liquid crystallinity may persist to a high concentration of the second component and, in fact, all over compositions if both components are mesomorphic [1–3].

Most binary mesophase systems exhibit mesophase-to-isotropic transition temperatures ($\mathbf{T}_c$) that are linearly dependent on composition; in some cases, however, there are exceptions.

In previous studies [2, 3], the effect of terminal substitution and inversion of the central –COO-group on the mesophase stability of unsymmetrically disubstituted phenyl benzoates and their binary, ternary, and quaternary mixtures were investigated.

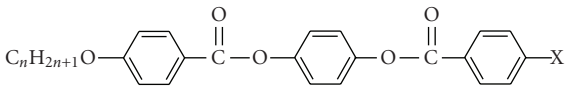
Introducing a second $–C_6H_4COO$-group to the phenyl benzoate molecule would definitely enhance the polarity and/or polarizability of the central part of the molecule and consequently of its mesophase stability. The p-phenylene-di-n-alkoxybenzoates have been shown to exhibit mesophases with broad ranges terminating at high temperatures [4–6], that is, higher clearing temperature (T_c) and mesomorphic range (ΔT), where, $\Delta T = T_c - T_m$. The introduction of very different alkoxy groups [7] or the replacement of one alkoxy end group by a polar (CH_3O, CH_3, Cl. CN., or NO_2) group [5] greatly affects the mesophase stability of the compound. Such systems would, therefore, be excellent for an extensive study of the effects of structural changes on the mesophase behaviour of their mixed systems.

The mesophase behaviour of binary mixtures of unsymmertically substituted 1,4-phenylene bis-(4-substituted benzoates) in which the two components differ from each other in the alkoxy-chain length [8] or in the polar substituent, X, was previously discussed [9]. In the latter mixtures the eutectic temperatures do not drop below 92°C for the mixtures of the chloro- with the methoxy-hexadecyloxy analogue, **I**6$_c$ with **I**6$_a$, [9]. Furthermore, the binary mixtures of the components each bearing an electron-withdrawing (Cl, CN, or NO_2) end group [9] as well as mixtures of homologues [8] do not show eutectic composition but show near ideal solution behaviour in the mixed solid, meso-, or liquid phase.

Table 1: Eutectic composition and phase transition temperatures (°C) of binary mixtures.

System A/B	n	4–$C_nH_{2n+1}O$–C_6H_4–COO–C_6H_4–OOC–C_6H_4–X–4 Composition (mol%) A	B	$T_{C–N}$	$T_{N–I}$ (found)	$T_{N–I}$ (calc.)
$I6_a/I6_b$	6	36.9	63.1	106.7	227.7	226.0
$I6_a/I6_c$		65.2	34.8	119.8	239.8	237.6
$I6_a/I6_d$		64.7	35.3	95.9	254.7	251.7
$I6_a/I6_e$		85.5	14.5	132.0	246.0	242.9
$I6_b/I6_c$		76.5	23.5	111.3	220.5	220.8
$I6_b/I6_d$		77.5	22.5	111.8	224.1	229.7
$I6_b/I6_e$		78.5	21.5	112.5	225.3	225.8
$I8_a/I8_b$	8	35.2	64.8	101.5	210.1	207.9
$I8_a/I8_c$		68.7	31.3	115.7	220.5	220.5
$I8_a/I8_d$		71.5	28.5	113.5	236.4	247.2
$I8_a/I8_e$		79.9	20.1	126.0	230.1	226.5
$I8_b/I8_c$		79.5	20.5	105.3	206.0	202.6
$I8_b/I8_d$		82.0	18.0	103.9	212.0	209.6
$I8_b/I8_e$		87.8	12.2	98.1	208.4	204.5
$I14_a/I14_b$	14	34.8	65.2	101.0	179.8	177.3
$I14_a/I14_c$		57.5	42.5	107.5	188.2	190.3
$I14_a/I14_d$		70.5	29.5	112.3	194.5	205.2
$I14_a/I14_e$		82.9	17.1	114.9	195.7	197.7
$I14_b/I14_c$		73.5	26.5	96.4	176.4	172.5
$I14_b/I14_d$		81.9	18.1	103.6	187.0	179.4
$I14_b/I14_e$		88.9	11.1	101.9	180.0	173.0

The objective of the present work is to investigate the mesophase behaviour in ternary mixtures of the previously prepared compounds [10], $I6_{a–e}$–$I14_{a–e}$ in an attempt to reduce, further, the melting point of their mixed solids:



I_{a-e}

n = 6 , 8 and 14 X = OCH_3, CH_3, Cl, NO_2 and CN

2. Experimental

All compounds prepared in this study were prepared according to the method previously described [10].

Ternary phase diagram was constructed for mixtures of components bearing substituents of different polarity but of the same alkoxy-chain length. Two types of phase diagrams were investigated for two different groups of ternary mixtures.

In the first group of ternary mixtures, A, each of the two of the three components bears an electron-donating group (CH_3O or CH_3) while the third component bears an electron-withdrawing group (Cl, CN, or NO_2). In the second group of ternary phase diagrams (group B), one component bears a methoxy (or methyl) group while each of the other two components bears an electron-withdrawing group. The method of investigating the eutectic composition differs from group A to group B. In group A, any two of the three components possess a eutectic point. In such case, the triangle of composition can be constructed according to the method described before [11], from which the eutectic composition of the ternary system is estimated, prepared, and characterized for its mesophase behaviour. This ternary eutectic composition can be, alternatively, verified by constructing the individual three phase diagrams starting with the eutectic mixtures of any two components and gradually adding the third component with a ratio varying between 0 and 100 mol%.

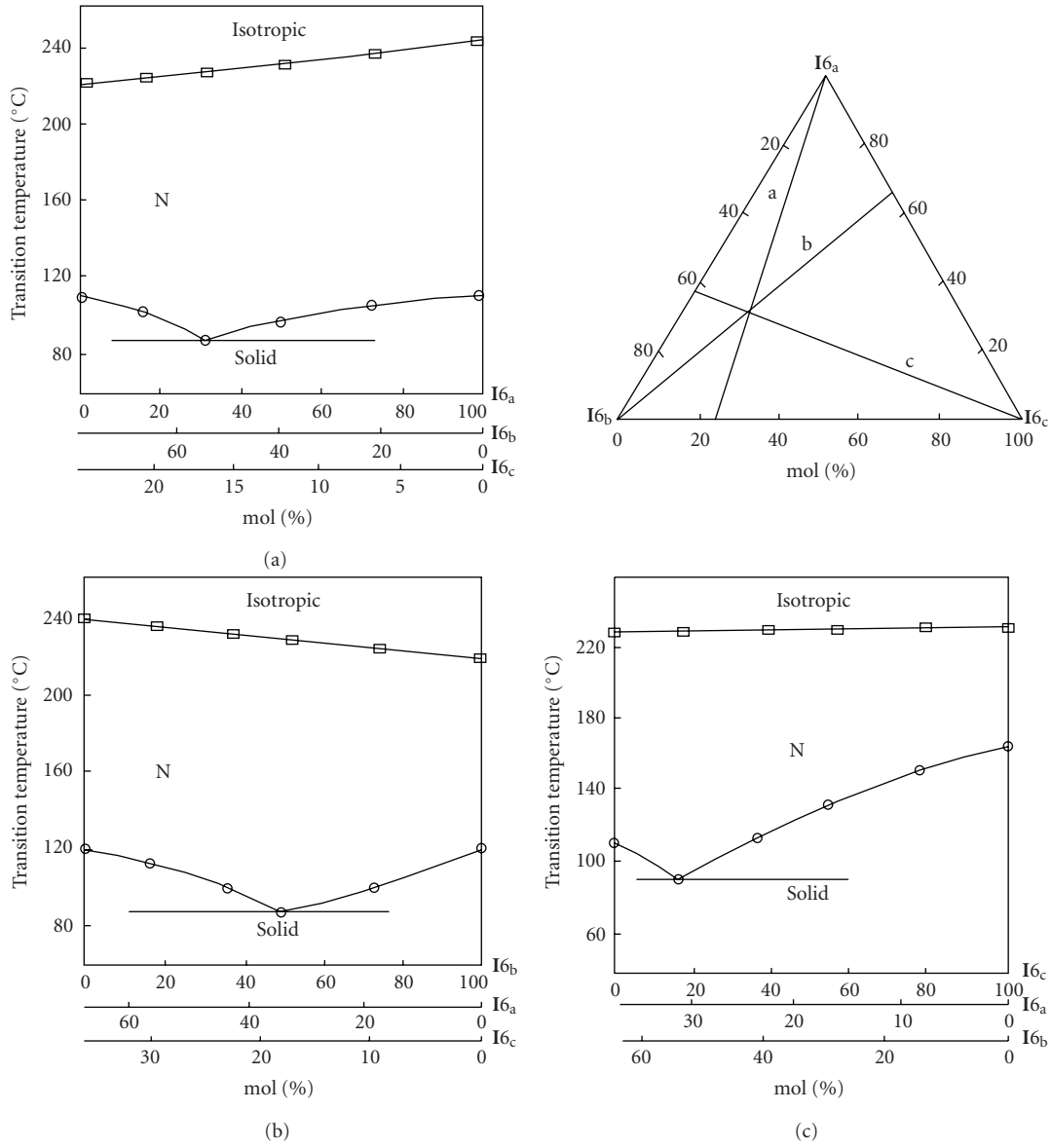


Figure 1: Composition triangle of the ternary system $\mathbf{I6}_a/\mathbf{I6}_b/\mathbf{I6}_c$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

In the second group of ternary mixtures, B, the binary mixtures of the two components bearing the electron-withdrawing substituent (Cl, CN, or NO2) do not possess a eutectic composition but form solid solution throughout the whole composition range of the two components. In such case, we cannot construct the triangle of composition. Alternatively, in group B ternary system, we can start with any of the eutectic mixtures of two components, one bearing an electron-donating and the other bearing an electron-withdrawing substituent, and adding the third that bears an electron withdrawing group. In this case, two ternary phase diagrams are thus constructed one confirms the other.

3. Results and Discussion

In order to estimate the eutectic composition of the ternary systems under investigation and consequently evaluate their phase behaviour, one should first determine the eutectic composition of all possible binary systems made from each pair of components in the concerned ternary system. These eutectic mixtures, with compositions as determined before [9], were prepared and their phase transition temperatures were measured by differential scanning calorimetry (DSC) and identified by polarized-optical microscopy. The results are summarized in Table 1. Some possible binary systems are missing in the table since their individual components

Table 2: Eutectic composition and phase transition temperatures (°C) of group A ternary mixtures.

System A/B/C	n	4–$C_nH_{2n+1}O$–C_6H_4–COO–C_6H_4–OOC–C_6H_4–X–4 Composition (mol%) A	B	C	$T_{C–N}$	$T_{N–I}$ (found)	$T_{N–I}$ (calc.)
$I6_a/I6_b/I6_c$	6	31.0	52.9	16.1	88.1	227.2	227.1
$I6_a/I6_b/I6_d$		31.1	53.0	15.9	84.2	232.0	236.2
$I6_a/I6_b/I6_e$		30.6	53.3	16.1	88.5	232.2	230.8
$I8_a/I8_b/I8_c$	8	30.2	55.8	14.0	86.3	227.0	208.8
$I8_a/I8_b/I8_d$		30.0	56.8	13.2	83.8	216.0	214.1
$I8_a/I8_b/I8_e$		33.6	58.3	8.1	84.3	216.5	210.8
$I14_a/I14_b/I14_c$	14	27.1	53.1	19.8	77.4	180.1	178.5
$I14_a/I14_b/I14_d$		29.2	58.3	12.5	80.1	184.5	183.6
$I14_a/I14_b/I14_e$		31.1	61.4	7.5	82.2	181.7	179.7

Table 3: Eutectic composition and phase transition temperatures (°C) of group B ternary mixtures.

System A/B/C	n	4–$C_nH_{2n+1}O$–C_6H_4–COO–C_6H_4–OOC–C_6H_4–X–4 Composition (mol%) A	B	C	$T_{C–N}$	$T_{N–I}$ (found)	$T_{N–I}$ (calc.)
$I6_a/I6_c/I6_d$	6	48.0	25.5	26.5	90.1	247.2	246.7
$I6_a/I6_c/I6_e$		58.6	31.4	10.0	92.5	234.0	239.5
$I6_a/I6_d/I6_e$		58.2	31.8	10.0	81.5	247.2	252.2
$I6_b/I6_c/I6_d$		61.0	21.0	18.0	86.3	227.0	230.3
$I6_b/I6_c/I6_e$		63.6	18.6	17.8	95.0	226.0	227.1
$I6_b/I6_d/I6_e$		63.5	18.5	18.0	86.3	232.5	234.5
$I8_a/I8_c/I8_d$	8	54.5	24.5	21.0	99.4	229.5	227.8
$I8_a/I8_c/I8_e$		53.0	24.0	23.0	94.1	227.5	224.8
$I8_a/I8_d/I8_e$		61.0	24.5	14.5	99.2	237.0	233.4
$I8_b/I8_c/I8_d$		67.8	17.2	15.0	80.5	214.0	210.5
$I8_b/I8_c/I8_e$		71.0	18.0	11.0	78.3	210.5	206.7
$I8_b/I8_d/I8_e$		73.8	16.2	10.0	75.3	217.0	212.6
$I14_a/I14_c/I14_d$	14	46.0	34.5	19.5	88.4	194.2	198.2
$I14_a/I14_c/I14_e$		52.0	37.0	11.0	86.0	195.1	192.9
$I14_a/I14_d/I14_e$		61.5	26.0	12.5	82.5	192.2	206.2
$I14_b/I14_c/I14_d$		63.0	23.1	13.9	88.0	186.0	180.6
$I14_b/I14_c/I14_e$		62.8	22.6	14.6	75.5	182.0	178.3
$I14_b/I14_d/I14_e$		67.6	16.0	16.4	86.0	192.0	185.4

form solid solution in each other. That is, the melting point of one component varies gradually from that of the first to that of the second component, thus, does not path a eutectic composition. It may also be noted that although some of the pure components are purely smectogenic ($I14_c$ and $I14_e$) or polymorphic ($I6_{d\&e}$ and $I8_{d\&e}$), all the binary eutectic mixtures, irrespective of their components, are only nematogenic.

3.1. Ternary Mixtures of Two Electron-Releasing (I_a and I_b) and One Electron-Withdrawing Substituted Compounds (I_c, I_d, or I_e): Group A Systems. In this group of ternary systems

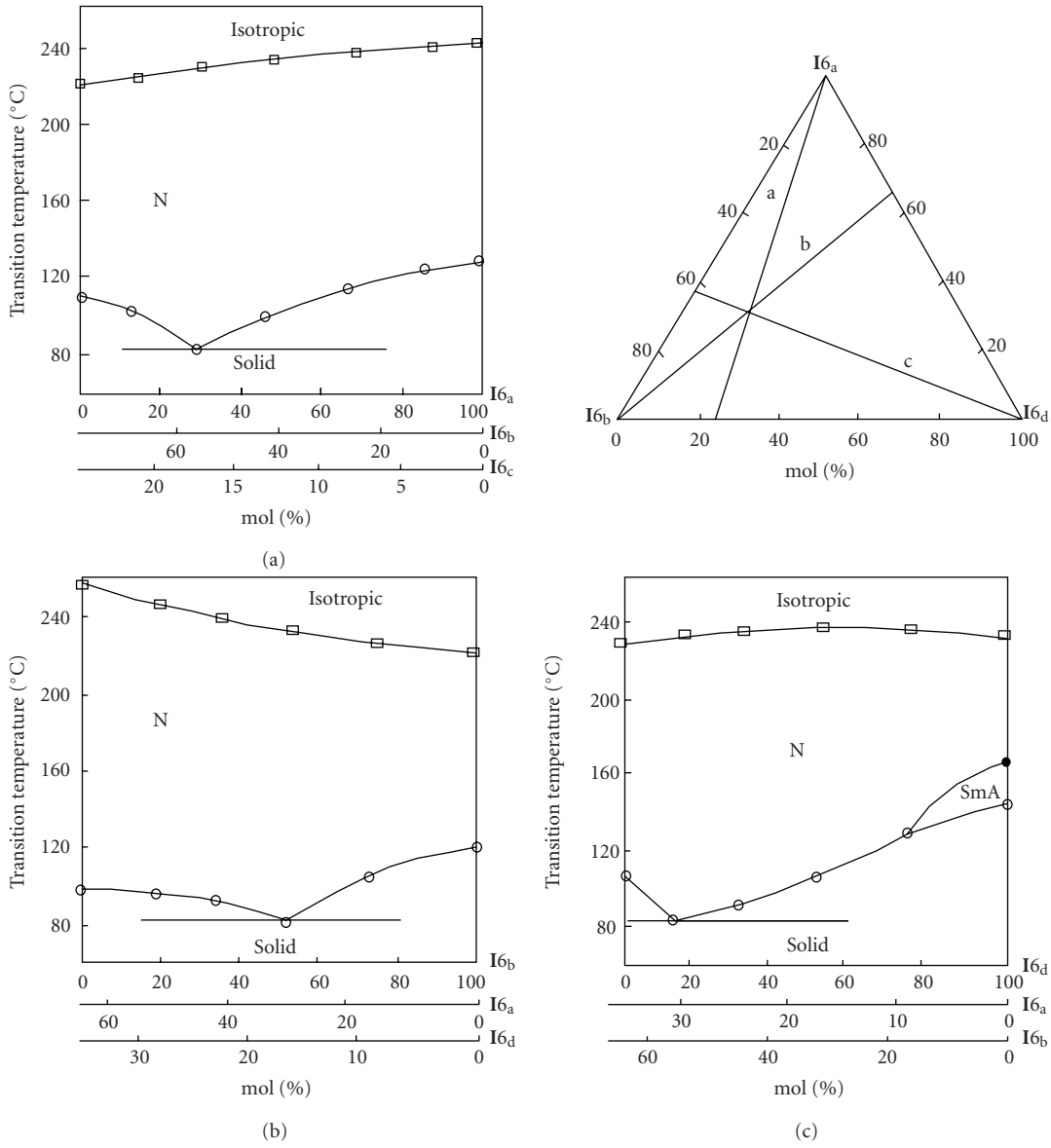


Figure 2: Composition triangle of the ternary system $\mathbf{I6}_a/\mathbf{I6}_b/\mathbf{I6}_d$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

(A/B/C) each pair of components (A/B, A/C, or B/C) form a binary system that possesses a eutectic composition. For such ternary systems, the composition of the mixtures is represented by an equilateral triangle. The composition triangle and phase diagrams of the nine possible ternary combinations were constructed, and are reproduced in Figures 1, 2, 3, 4, 5, 6, 7, 8, and 9. In each case, the composition triangle is constructed by locating each of the eutectic compositions of the three individual binary mixtures on its corresponding side and connecting each one to the opposing apex (representing the pure third component). The point of intersection of the three inner connecting lines (a, b, and c) gives the eutectic composition of the system concerned. For each composition triangle, that is, a given ternary system, three phase diagrams covering the composition ranges represented by the inner lines a, b, and c are produced.

As can be seen from Figures 1–9, the eutectic composition of any ternary system can be safely determined either from any one of the phase diagrams a, b, or c or from the point of intersection of the three inner lines inside the composition triangle. The composition and phase transition temperatures of the eutectic mixtures are collected in Table 2. It can be seen from Figure 1(a) that the gradual addition of the methoxy compound $\mathbf{I6}_a$ to the eutectic mixture of the chloro ($\mathbf{I6}_c$) with the methyl ($\mathbf{I6}_b$) derivatives

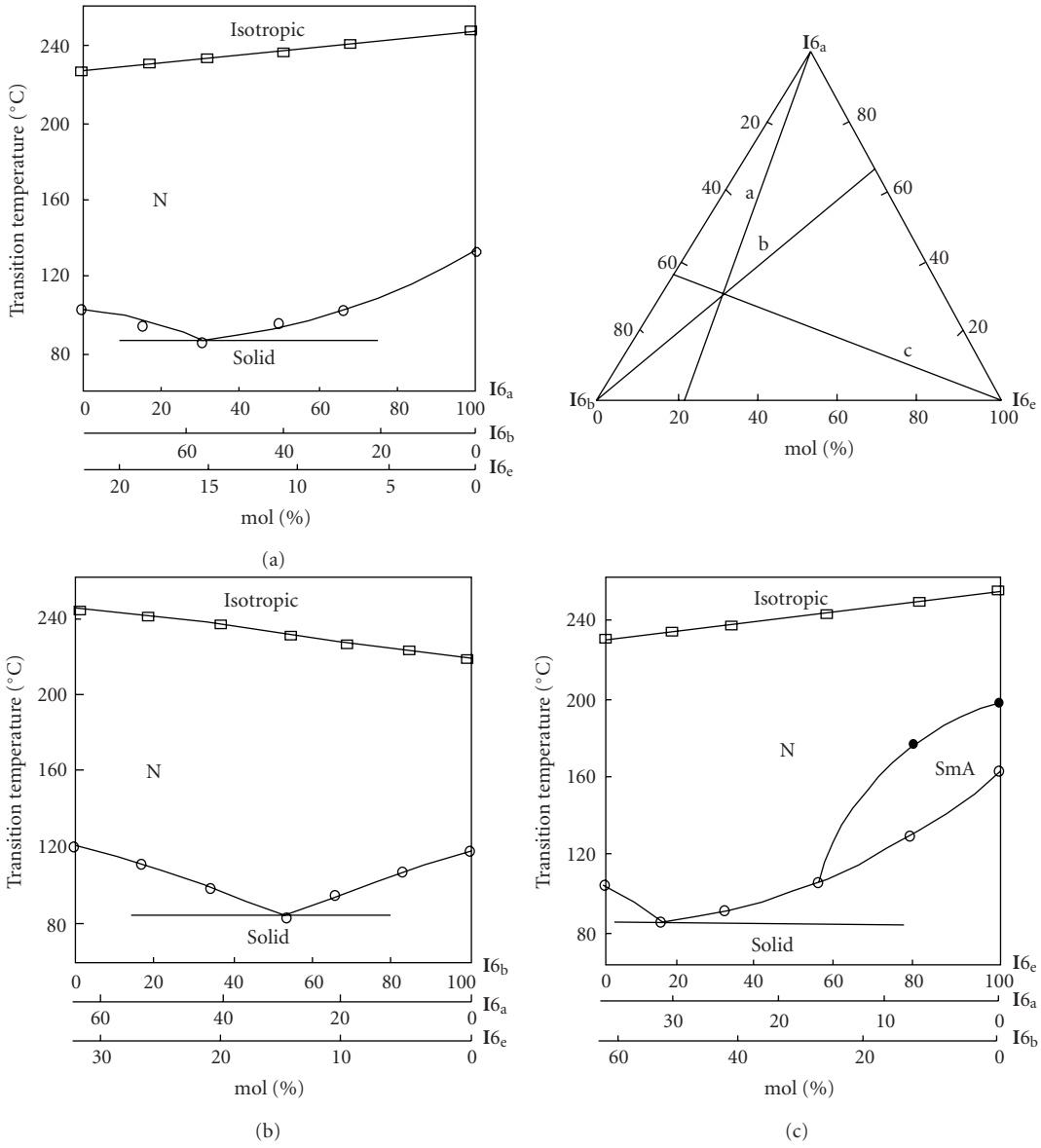


FIGURE 3: Composition triangle of the ternary system $\mathbf{I}6_a/\mathbf{I}6_b/\mathbf{I}6_e$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

results in a linear $\mathbf{T}_c$-composition dependence. The other two sequences of addition (Figures 1(b) and 1(c)) behave similarly indicating the formation of ideal solutions from the three components $\mathbf{I}6_a$, $\mathbf{I}6_b$, and $\mathbf{I}6_c$. Similar behaviors were observed for the **I**8 (Figure 4) and **I**14 (Figure 7) similar analogues.

On the other hand, the addition of the cyano ($\mathbf{I}6_d$) derivative to the eutectic mixture of $\mathbf{I}6_a$ with $\mathbf{I}6_b$ results in a slight enhancement of the nematic-isotropic transition temperature (Figure 2(c)). The reverse seems true: that is, the addition of the methyl compound ($\mathbf{I}6_b$) to the eutectic mixture of the methoxy ($\mathbf{I}6_a$) and cyano ($\mathbf{I}6_d$) compounds results in $T_{N–I}$ values lower than those expected from the linear dependence (compare curve b in the same group of figures). This may be attributed to the stronger forces of association between the cyano substituted analogue and the methoxy analogue compared with those occurring between the methyl and methoxy derivatives.

For the higher homologues **I**14, the addition of the cyano ($\mathbf{I}14_d$) to the eutectic mixture of the methyl ($\mathbf{I}14_b$) with the methoxy ($\mathbf{I}14_a$) results in a linear $\mathbf{T}_c$-composition dependence up to 70 mol% of $\mathbf{I}14_d$, followed by a nonlinear $\mathbf{T}_c$-composition dependence (Figure 8(c)). Similar phase behavior was observed upon the addition of the nitro analogue ($\mathbf{I}14_e$) to the eutectic mixture, $\mathbf{I}14_a/\mathbf{I}14_b$, (Figure 9(c)).

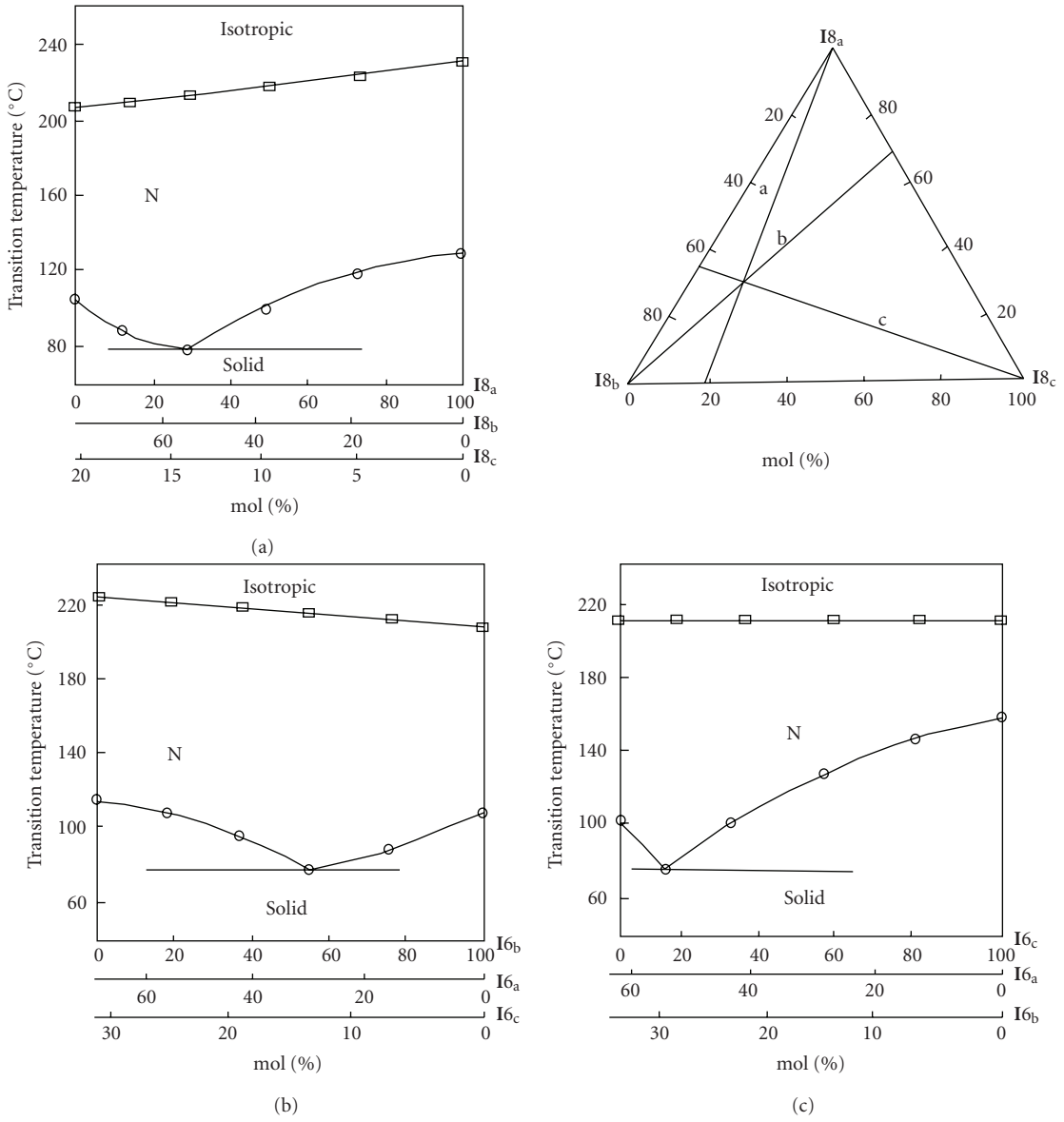


Figure 4: Composition triangle of the ternary system $\mathbf{I}8_a/\mathbf{I}8_b/\mathbf{I}8_c$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

With respect to the reverse addition of the methoxy ($\mathbf{I}14_a$) or the methyl ($\mathbf{I}14_b$) to the eutectic mixtures of the cyano, $\mathbf{I}14_d$, (Figures 8(a) and 8(b)) or nitro, $\mathbf{I}14_e$, (Figures 9(a) and 9(b)) with the third component, $\mathbf{T}_c$ was found to vary almost linearly with composition.

Phase diagrams of the mixtures of the intermediate analogues $\mathbf{I}8_{a–e}$, (Figures 5 and 6) showed near linear $\mathbf{T}_c$-composition dependences with a composition range of smectic A phase when the $\mathbf{I}8_d$ or $\mathbf{I}8_e$ is added to the eutectic mixture of $\mathbf{I}8_a/\mathbf{I}8_b$., respectively.

3.2. Ternary Mixtures of One Electron-Releasing ($\mathbf{I}_a$ or $\mathbf{I}_b$) and Two Electron-Withdrawing Substituted Compounds ($\mathbf{I}_c$, $\mathbf{I}_d$, or $\mathbf{I}_e$): Group B Systems. In this group of ternary systems, only two of the three possible binary mixtures, those containing the electron donating substituted analogue, either $\mathbf{I}_a$ or $\mathbf{I}_b$ together with one of the electron withdrawing substituted analogues, $\mathbf{I}_c$, $\mathbf{I}_d$, or $\mathbf{I}_e$, possess the eutectic composition. The third possible binary system is that of two electron withdrawing substituted analogues and behaves ideally through the formation of solid solution in the solid and mesomorphic phases. So, the composition triangle cannot be constructed, as done for group A. Alternatively we can construct two parallel phase diagrams for the ternary system, starting with the eutectic composition of either of the binary systems and adding the third pure component of the

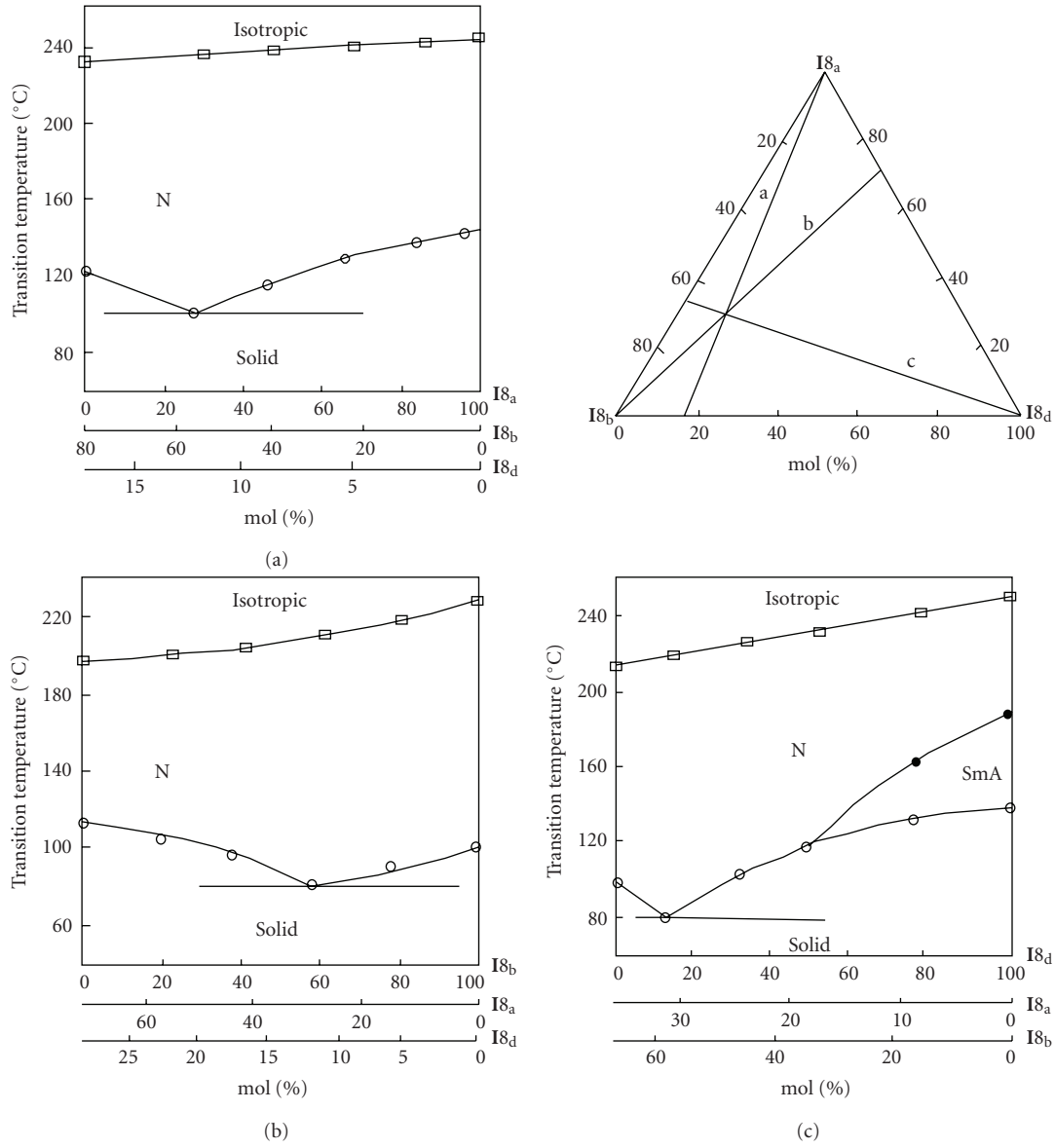


Figure 5: Composition triangle of the ternary system $\mathbf{I}8_a/\mathbf{I}8_b/\mathbf{I}8_d$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

other electron withdrawing substituted analogue. These two ternary-phase diagrams can be constructed for each of group B ternary systems. Eutectic composition and phase transition temperatures of group B ternary mixtures are given in Table 3 and representative figures are reproduced for the possible ternary mixtures of the I6 analogues (Figure 10).

3.3. Depndence of $\mathbf{T}_c$ *Values of the Ternary Eutectic Mixtures on the Polarizability Anisotropy of the* C_{Ar}*–X Bonds.* We are going here to apply the relation derived by van der Veen [12] to study the dependence of the clearance temperature, $\mathbf{T}_{N–I}$, on the anisotropy of polarizability, $\Delta\alpha_X$, of bonds to small, compact terminal substituents, X, and extended later by Naoum et al. [11] to cover binary, ternary, and quaternary mixture. The linear dependences, which differ according to the alkoxy-chain length, were analyzed [10] by the method of least squares to give the three regression lines for series **I**6, **I**8, and **I**14, respectively:

$$\begin{aligned}
\mathbf{T}_c(\mathbf{I}6) &= 20.73 + 5.50 \times 10^{39}\,\Delta\alpha_X,\\
\mathbf{T}_c(\mathbf{I}8) &= 20.27 + 5.71 \times 10^{39}\,\Delta\alpha_X,\\
\mathbf{T}_c(\mathbf{I}14) &= 19.30 + 6.61 \times 10^{39}\,\Delta\alpha_X.
\end{aligned} \tag{1}$$

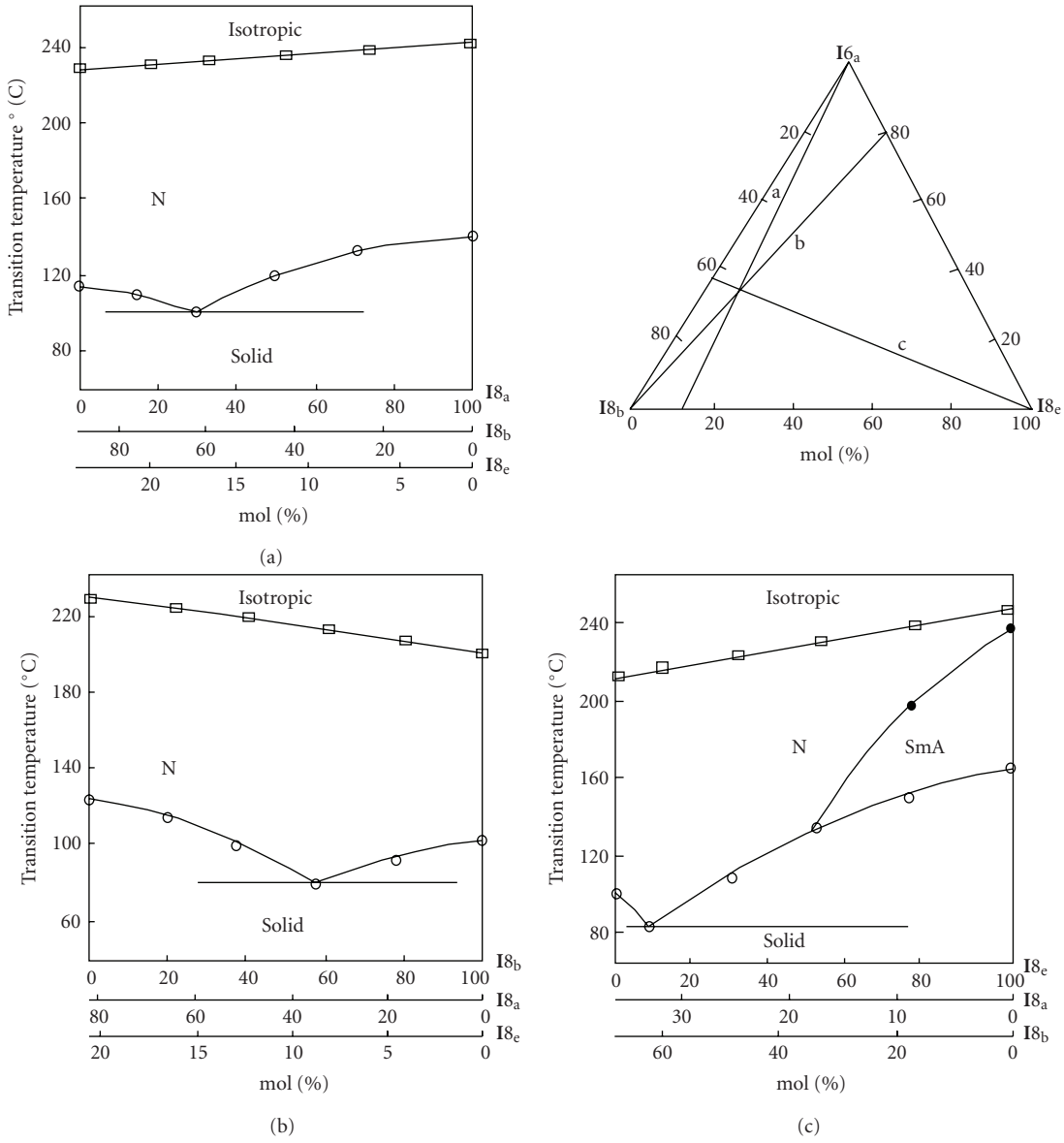


Figure 6: Composition triangle of the ternary system $\mathbf{I}8_a/\mathbf{I}8_b/\mathbf{I}8_e$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

Equations (1) was used to calculate the anisotropic transition temperatures, T_c, for the eutectic mixtures of the three-component systems investigated, using the mixture law (2), and the results were included in their corresponding tables:

$$\mathbf{T}_c = \Sigma\chi_{(i)}\mathbf{T}_{N-I(i)} \tag{2}$$

$$= \Sigma\chi_{(i)}\left(\Delta\alpha_M + \rho\Delta\alpha_{X(i)}\right)^2, \tag{3}$$

where $\chi_{(i)}$ is the mole fraction of the component "i," $\Delta\alpha_M$ is the polarizability anisotropy of the molecular structure(**I**6, **I**8, or **I**14) excluding the substituent X, and $\Delta\alpha_{X(i)}$ and ρ are the polarizability anisotropy of the bond and the slope of the regression line of the concerned series, respectively. The values of $\Delta\alpha_{X(i)}$ for the derivatives investigated were given elsewhere [13].

Equation (3) was used to calculate the $\mathbf{T}_c$ values for the eutectic mixtures of the binary and ternary systems under investigation, and the results of computation are added to Tables 1, 2, and 3, as appropriate. As can be seen from Table 1, except for the systems consisting of pure smectogenic components, $\mathbf{I}14_d$ and $\mathbf{I}14_e$, the calculated $\mathbf{T}_c$ values were found to agree to great extent with the experimental results. These findings reflect the applicability of such relations to our investigated compounds where no complex formation was observed between components in their binary systems. In cases where the smectogenic compound, $\mathbf{I}14_d$ or $\mathbf{I}14_e$,

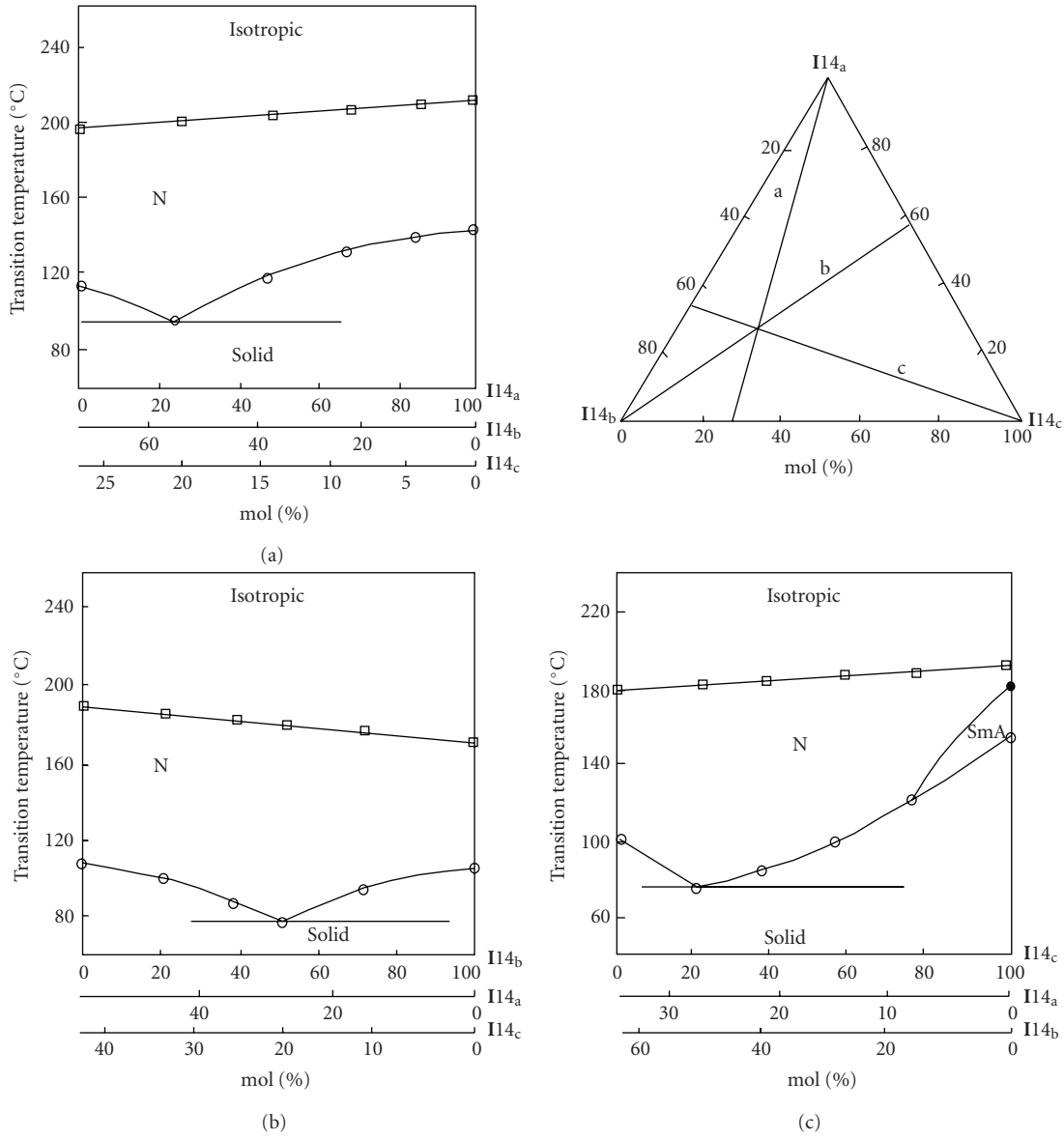


FIGURE 7: Composition triangle of the ternary system $\mathbf{I}14_a/\mathbf{I}14_b/\mathbf{I}14_c$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

is mixed with a nematogene or polymorphic derivative, a complex phase diagram is obtained and the $\mathbf{T}_c$ calculated differs from those measured.

Comparison of the corresponding values for group A ternary systems (Table 2) revealed that in the case of the lowest homologues (**I**6) investigated, addition of the chloro derivative ($\mathbf{I}6_c$) to the binary mixture of the methoxy ($\mathbf{I}6_a$) with the methyl ($\mathbf{I}6_b$) derivatives results in a nearly linear ideal behavior; that is, results agree within 0.1°C. Whereas, addition of the cyano ($\mathbf{I}6_d$), or the nitro ($\mathbf{I}6_e$) analogue, to the same binary system is accompanied by a decrease in $\mathbf{T}_c$ by 4.2°C or enhancement by 1.4°C, respectively. This, in turn, reflects the tendency towards complex formation between the electron-deficient nitro derivative, $\mathbf{I}_e$, and the electron-rich methoxy or methyl analogue, $\mathbf{I}_a$ or $\mathbf{I}_b$. And the nitro derivative is more efficient in promoting complex formation compared with its cyano analogue. As for the higher homologues, **I**8 and **I**14, the measured $\mathbf{T}_c$ values are always greater than the calculated ones reflecting the increased affinity towards complex formation as the length of the alkoxy side chain is increased. In addition, the complexity of the phase diagrams (see Figures 8 and 9) adds extra role to the nonideal behavior.

Turning now to group B ternary systems (Table 3), again in the lowest homologues (**I**6), except for the first system ($\mathbf{I}6_a/\mathbf{I}6_c/\mathbf{I}6_d$), **I** all five systems of the measured

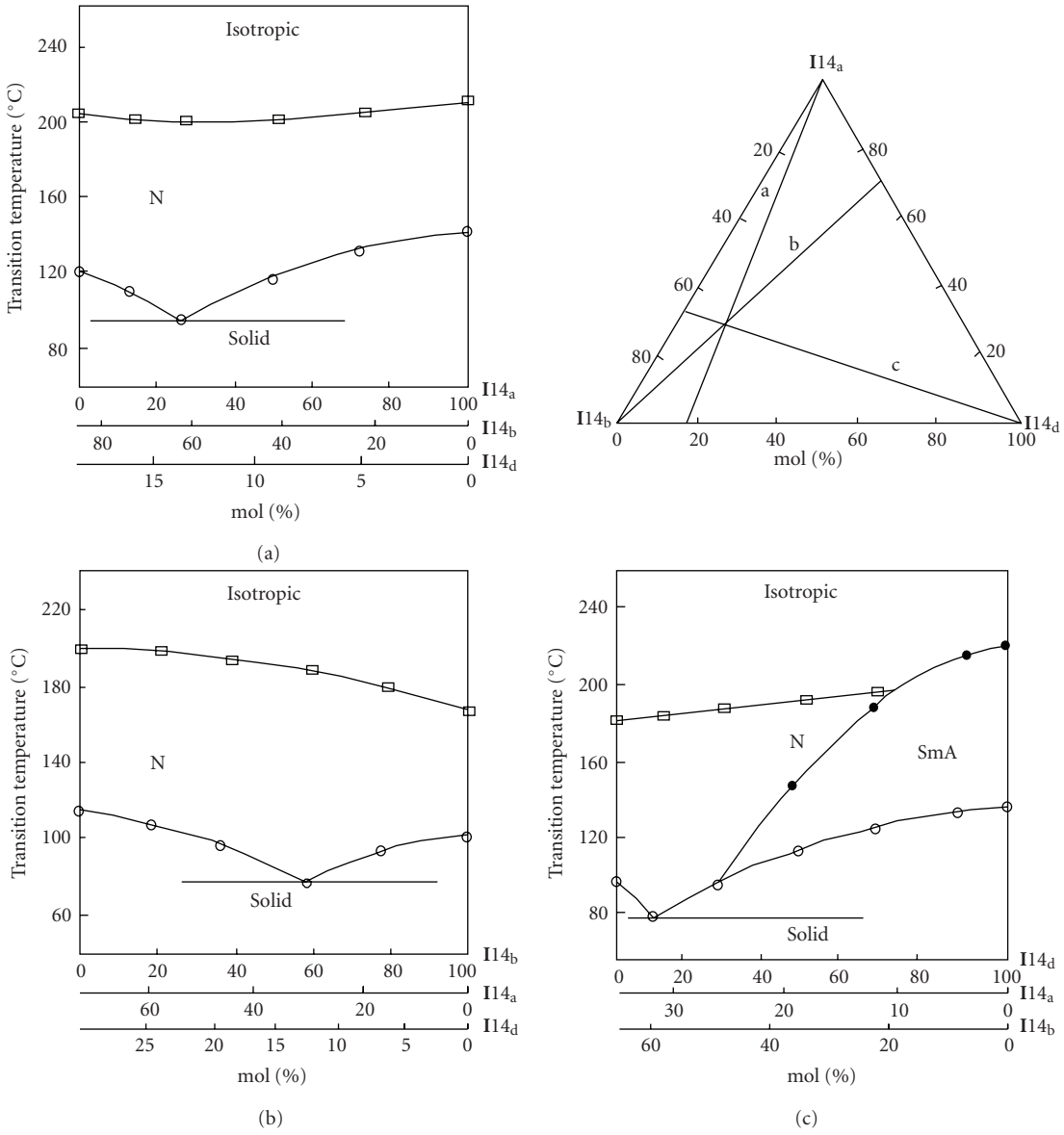


FIGURE 8: Composition triangle of the ternary system $\mathbf{I}14_a/\mathbf{I}14_b/\mathbf{I}14_d$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

values showed negative deviation from calculated ones. In the intermediate homologues (**I**8), all systems showed enhancement of the measured $\mathbf{T}_c$ values over the calculated ones. The irregularity observed between the measured and calculated $\mathbf{T}_c$ values in the highest homologues (**I**14) can be attributed to the nonhomogeneity of components (smectic or nematic) forming the ternary system (see Table 3 and Figure 10).

4. Conclusion

Five homologous series of the family compounds, unsymmetrical 1,4-phenylene bis-(4-substitutedbenzoates), were prepared and characterized for their phase behavior, by DSC and POM, in pure and mixed states. Two types of substituents were used, namely, an alkoxy group of variant length (6, 8, and 14 carbons) and a compact polar group (X = CH_3O, CH_3, Cl, NO_2, and CN). Ternary mixtures were independently prepared, from various analogues bearing different substituents, X, but of the same alkoxy chain length, and similarly characterized for their phase behavior. Two groups of ternary phase diagrams were investigated, dependent upon the difference in the polarity of the substituent, X, which was found to affect the miscibility in the binary solid mixtures. In the first group A, each of the two of the components bears an electron donating, (CH_3O or CH_3), group, while the third component bears an electron

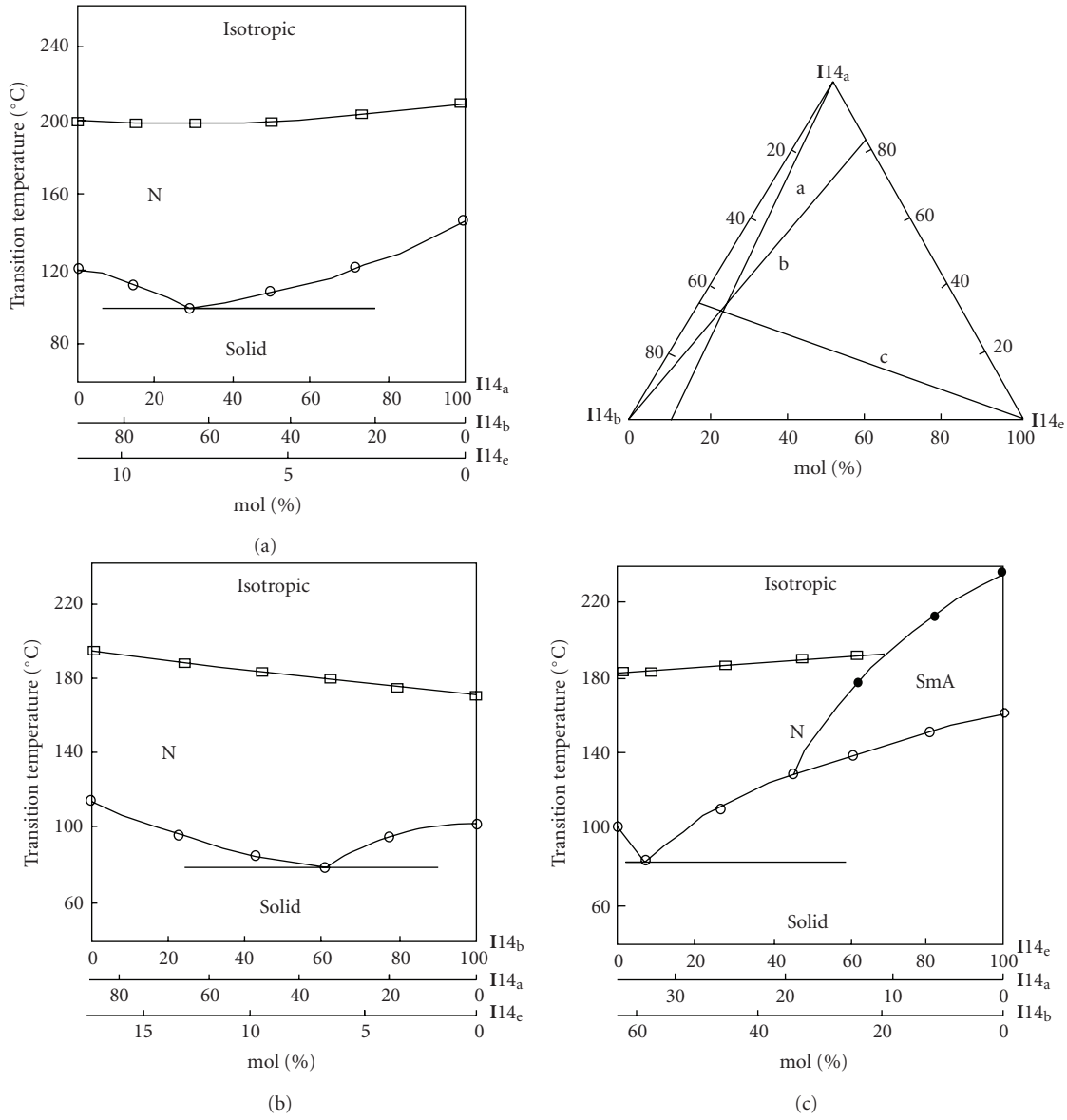
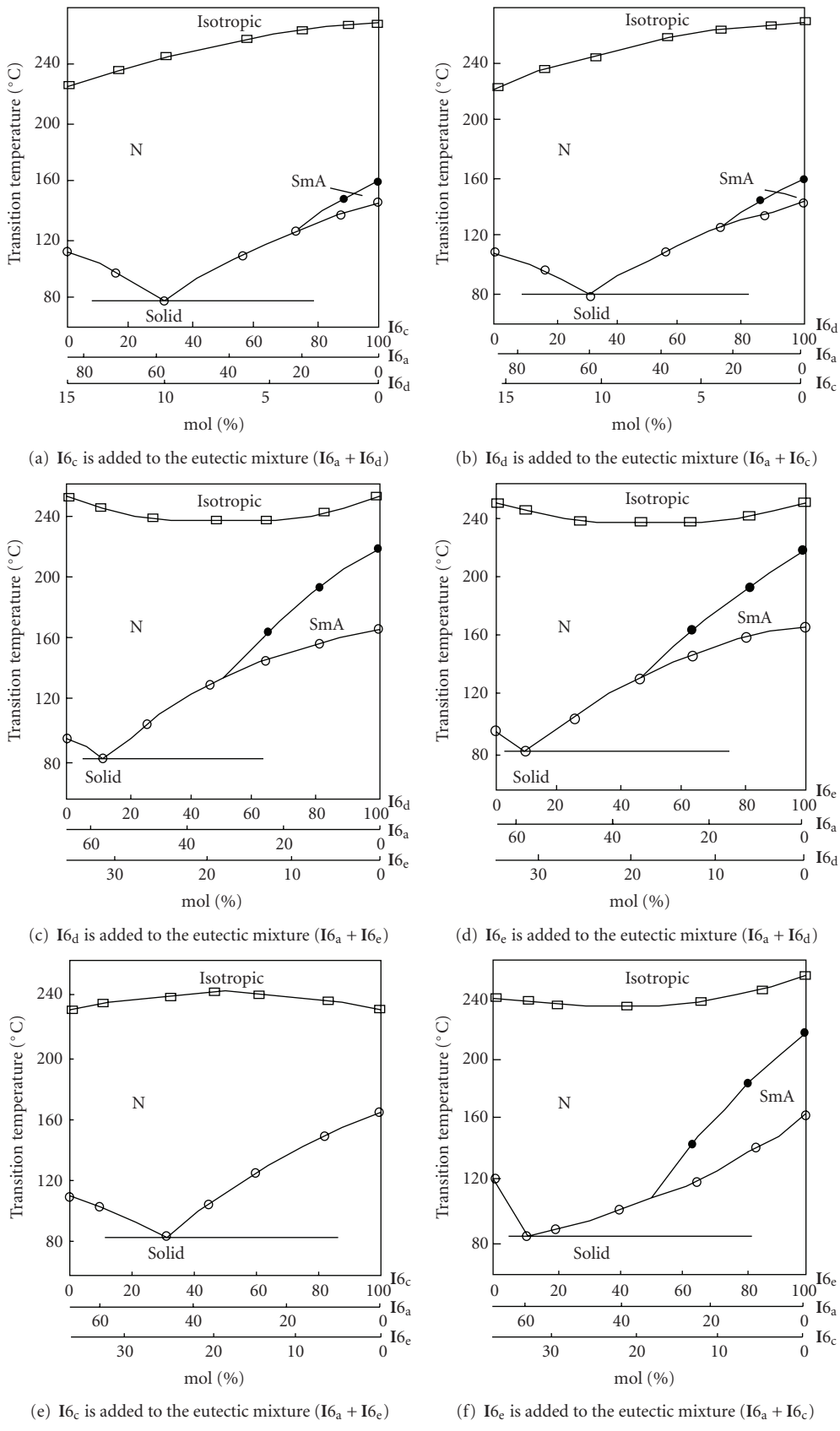


FIGURE 9: Composition triangle of the ternary system $\mathbf{I}14_a/\mathbf{I}14_b/\mathbf{I}14_e$ and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

withdrawing (Cl, NO_2, or CN) group. In this case, any binary mixture made from two of the three components was found to possess a eutectic composition, and consequently, the triangle of composition could be constructed and the ternary eutectic composition be deduced. In group B, each of ternary mixtures, two from the three components, bears an electron withdrawing group and the third bears an electron-donating group. In the later case, one from the three possible binary mixtures does not pass a eutectic composition; instead it forms solid solution. Hence, the ternary eutectic composition is elucidated from the phase diagram constructed by adding the third component to the eutectic mixture of the other two.

For both groups of phase diagrams (A and B) ternary eutectic compositions were obtained. On the other hand, the T_c-composition dependences were found to depend on the differences in polarity of the substituent carried by each of the individual components. That is, (i) linear dependency was observed in mixtures that do not lead to disturbances in the molecular association, (ii) positive deviation is observed from linearity in cases when the added component enhances molecular association, (iii) negative deviation is observed if the added component slightly disrupts association, and (iv) complex variation is observed in cases where the third component is polymorphic, possessing SmA and N mesophases ($\mathbf{I}14_d$ and $\mathbf{I}14_e$).



(a) $\mathbf{I6_c}$ is added to the eutectic mixture ($\mathbf{I6_a} + \mathbf{I6_d}$)

(b) $\mathbf{I6_d}$ is added to the eutectic mixture ($\mathbf{I6_a} + \mathbf{I6_c}$)

(c) $\mathbf{I6_d}$ is added to the eutectic mixture ($\mathbf{I6_a} + \mathbf{I6_e}$)

(d) $\mathbf{I6_e}$ is added to the eutectic mixture ($\mathbf{I6_a} + \mathbf{I6_d}$)

(e) $\mathbf{I6_c}$ is added to the eutectic mixture ($\mathbf{I6_a} + \mathbf{I6_e}$)

(f) $\mathbf{I6_e}$ is added to the eutectic mixture ($\mathbf{I6_a} + \mathbf{I6_c}$)

Figure 10: Ternary phase diagrams of the systems.

References

[1] M. M. Naoum, G. Hohne, H. Seliger, and E. Happ, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures. I. 4-hexadecyloxyphenyl-4-carboxybenzoate and 4-carboxyphenyl-4-hexadecyloxybenzoate," *Liquid Crystals*, vol. 23, no. 5, pp. 653–658, 1997.

[2] M. M. Naoum, G. R. Saad, R. I. Nessim, T. A. Abdel-Aziz, and H. Seliger, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures. II. 4-hexadecyloxyphenyl arylates and aryl 4-hexadecyloxy benzoates," *Liquid Crystals*, vol. 23, no. 6, pp. 789–795, 1997.

[3] M. M. Naoum, G. R. Saad, R. I. Nessim, and T. A. Abdel-Aziz, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures III. Binary mixtures of alkoxyphenyl arylates and arylalkoxybenzoates," *Liquid Crystals*, vol. 25, no. 2, pp. 165–173, 1998.

[4] M. J. S. Dewar and J. P. Schroeder, "p-Alkoxy- and p-carbalkoxybenzoates of diphenols. A new series of liquid crystalline compounds," *Journal of Organic Chemistry*, vol. 30, no. 7, pp. 2296–2300, 1965.

[5] M. J. S. Dewar and R. S. Goldberg, "Role of p-phenylene groups in nematic liquid crystals," *Journal of the American Chemical Society*, vol. 92, no. 6, pp. 1582–1586, 1970.

[6] S. L. Arora, J. L. Fergason, and T. R. Taylor, "Molecular structure and liquid crystallinity. Phenylene bis(alkoxybenzoates)," *Journal of Organic Chemistry*, vol. 35, no. 12, pp. 4055–4058, 1970.

[7] S. A. Haut, D. C. Schroeder, and J. P. Schroeder, "Liquid crystals. II. Unsymmetrical p-phenylene di-p-n-alkoxybenzoates," *Journal of Organic Chemistry*, vol. 37, no. 9, pp. 1425–1428, 1972.

[8] M. M. Naoum, R. I. Nessim, G. R. Saad, and T. Y. Labeeb, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures XII. Binary mixtures of homologues of unsymmetrical 1,4-phenylene bis(4-substituted benzoates)," *Liquid Crystals*, vol. 30, no. 2, pp. 165–172, 2003.

[9] M. M. Naoum, R. I. Nessim, G. R. Saad, and T. Y. Labeeb, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures XI. Binary mixtures of unsymmetrical 1,4-phenylene bis-(4-substituted benzoates)," *Liquid Crystals*, vol. 29, no. 7, pp. 929–943, 2002.

[10] M. M. Naoum, T. Y. Labeeb, E. Happ, and H. Seliger, "Effect of molecular structure on the phase behavior of some liquid crystalline compounds and their mixtures X. Unsymmetrical 1,4-phenylene-bis-(4-substituted benzoates)," *Thermochimica Acta*, vol. 391, no. 1-2, pp. 151–158, 2002.

[11] M. M. Naoum, A. A. Mansour, and A. A. Bayoumy, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures VII. Ternary mixtures of enantiotropes," *Liquid Crystals*, vol. 27, no. 2, pp. 243–247, 2000.

[12] J. Van der Veen, "The influence of terminal substituents upon the nematic-isotropic transition temperature," *Journal de Physique Colloques*, vol. 36, pp. C1-375–C1-377, 1975.

[13] M. M. Naoum, R. I. Nessim, G. R. Saad, and T. A. Abdel-Aziz, "Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures IV. Dependence of Tc on the anisotropy of polarizability of the aryl-X bond," *Liquid Crystals*, vol. 25, no. 1, pp. 73–83, 1998.