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Effect of exchange of terminal substituents on the mesophase behavior of laterally methyl substituted phenyl azo benzoates in pure and mixed systems

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ABSTRACT

Two groups of the formulae, 4-(4'-hexyloxy)phenylazo-2-(and 3)methyl phenyl-4"-substituted benzoates (I_{a-e} and II_{a-e}) were prepared and investigated for their mesophase behavior. Each group consists of five derivatives that differ from each other by the terminal polar substituent *X* which varies between CH₃O, CH₃, Br, NO₂, and CN. Two other isomeric groups, III_{a-e} and IV_{a-e} , that exchange the terminal substituents, *X* and C₆H₁₃O, were also prepared and similarly characterized. Four different types of binary phase diagrams were constructed in which both components are corresponding isomers one from each of the four groups (I–IV). In the two binary mixtures, I/II and III/IV, the two components are positional isomers that differ in the position of the lateral methyl group, while in the other two systems, I/III and II/IV, the two components are again positional isomers that exchange the two wing substituents. The study is undertaken to investigate the effect of exchange of the terminal substituents on the mesomorphic properties of the produced derivatives in their pure or mixed states.

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1. Introduction

Generally polar substituents, through mesomeric interactions with the mesogenic portion of the molecule, affect the polarizability of the aromatic ring to which they are attached. Compact, polar, and/or polarizable groups appear to be very effective in creating mesophases with relatively high stability [1]; that is, extending upward the temperature region for the persistence of the mesophase. This has been attributed [1–4] to the increase of intermolecular attraction with the increase of polarity and/or polarizability due to substitution. In the phenyl benzoate ester system, the mesomorphic phase becomes more persistent when the mesophase stability effect of the mutual conjugation between the terminal substituent and the ester carbonyl is increased. In previous works [5-7], the effect of exchange of the terminal substituents on the mesophase behavior of two groups of the phenyl benzoate derivatives, namely, 4-alkoxyphenyl-4'-substituted benzoates and 4-substituted phenyl-4'-alkoxybenzoates, as well as of their binary mixtures, was investigated. Molecules of these types represent extremes in the conjugative interactions between the terminal substituent and the remainder of the molecule. Thus, while electron-donating substituents promote the polarity of the ester carbonyl group, which in turn results in stronger intermolecular attractions, electron-withdrawing substituents, which are situated in a para position with respect to the ester-oxygen atom, reduce the polarity of the carbonyl group, and hence, lower the clearing point of the mesophase. In another work [8], the exchange of the two terminal carboxy and hexadecyloxy groups attached to the two opposite sides of the phenyl benzoate molecule, were found to affect the stability of the mesophase to variable extents due to differences in the mesomeric interaction in either case.

In view of the high mesophase stability of a three-ring molecule compared with a two-ring one, it seems interesting to investigate the effect of exchange of the two wing substituents attached to the three-ring phenylazo phenyl benzoate molecule on the mesophase behavior of the resulting isomers. The azo-ester molecule was chosen on the basis of its relatively higher mesophase stability. Dye-containing materials, on the other hand, are applied to a wide variety of fields such as high technology and nano-technology [9]. On the other hand, the introduction of the lateral-methyl group into either position (2 or 3) of the central benzene ring is an attempt to reduce the melting point of the laterally-neat analogues. In this respect, two groups of laterally methyl substituted arylazophenyl-4-alkoxy benzoates were investigated [10] for their mesophase behavior. All members of the first group, in which the methyl group is introduced into position-2 of the central benzene ring, were found to be purely nematogenic, but of little stability compared with their laterally-neat analogues. In the second group, where the methyl group is introduced this time into position-3, the orientation of the methyl group is not in favor of mesphase stability so

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that it destabilizes the nematic phase. In both cases, extension of the alkoxy chain gives rise to a decrease in the nematic stability.

The present study aims to investigate, first, the effect of the methyl-lateral substitution into the central benzene ring of the previously investigated azo-ester [10], but with shorter alkoxy-chain length (n = 6) which is expected to be of higher nematic stability (series III_{a-e} and IV_{a-e}). Secondly, it is to investigate the effect of exchange of the two wing substituents ($C_6H_{13}O$ and X) on the mesophase behavior of the resulting isomers (Groups I_{a-e} and II_{a-e}).



(\mathbf{I}_{a-e})

I_a, X=CH₃O, I_b, X=CH₃, I_c, X=Br, I_d, X=NO₂, and I_e, X=CN.





II_a, X=CH₃O, II_b, X=CH₃, II_c, X=Br, II_d, X=NO₂, and II_c, X=CN.



 (III_{a-e})

III_a, X=CH₃O, III_b, X=CH₃, III_c, X=Br, III_d, X=NO₂, and III_e, X=CN.



IV_a, X=CH₃O, IV_b, X=CH₃, IV_c, X=Br, IV_d, X=NO₂, and IV_e, X=CN.

A third aim is to investigate the effect of steric interaction, on the binary phase behavior, that may be encountered between any two corresponding positional isomers, once based on different methyl-protrusion (I/II and III/IV), and another between alternatively wing-substituted isomers (I/III and II/IV).

2. Experimental

Chemicals have been purchased from the following companies: Aldrich, Wisconsin, USA; E. Merk, Darmstadt, Germany; and Fluka, Buchs, Switzerland.

2.1. Preparation of materials

Compounds I_{a-e} and II_{a-e} were prepared according to Scheme 1:

While their terminally substituted isomers, III_{a-e} and IV_{a-e} , were prepared according to Scheme 2:

2.1.1. Preparation of 4-(4'-hexyloxy phenylazo)-2-(or 3-)methyl phenol (**A**)

One molar equivalent of the 4-hexyloxy aniline in ice-cold dilute hydrochloric acid was diazotized with cold sodium nitrite solution and then added slowly to a cold 2-(or 3-)cresol/sodium hydroxide solution (1:1). The solid azo product was filtered and crystallized twice from ethanol. The melting points of the prepared azo dyes are 93.1 and 88.2 °C, respectively.

2.1.2. Preparation of 4-(4'-substituted phenylazo)-2-(or 3)-methyl phenol (**B**)

These were prepared in a similar manner from 4-substituted aniline and 2-(or 3-) cresol. The melting points of the prepared azo dyes were in good agreement with those reported in literature [11].

2.1.3. Preparation of 4-(4'-hexyloxy phenylazo)-2-(or

3)-methylphenyl-4"-substituted benzoates, I_{a-e} and II_{a-e}

Molar equivalents of the 4-(4'-hexyloxy phenylazo)-2-(or 3-) methyl phenol (**A**) and 4-substituted benzoic acid were dissolved in dry methylene chloride. To the resulting solution, 2-molar equivalents of dicyclohexyl carbodiimide (DCC) and few crystals of 4-(dimethylamino) pyridine (DMAP), as catalyst, were added and the solution left to stand for 72 h at room temperature with stirring. The solid separated was then filtered off and the solution evaporated. The obtained solid residue was crystallized twice from ethanol to give TLC pure products, as indicated by one spot in their TLC thermograms.

2.1.4. Preparation of 4-(4'-substituted phenylazo)-2-(or

3)-methylphenyl-4"-n-hexyl oxy benzoates, III_{a-e} and IV_{a-e}

These were similarly prepared using the phenols (**B**) and 4-*n*-hexyloxy benzoic acid.



Scheme 1. Steps for the preparation of compounds I_{a-e} and II_{a-e} .

2.2. Physical characterization

Calorimetric measurements were carried out on a PL-DSC of Polymer Laboratories, Epsom Surrey, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga, et al. [12]. Measurements were carried out for small samples (2–3 mg) placed in sealed aluminum pans. All of the thermograms have been achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (10 mL/min).

Transition temperatures were checked and types of mesophases identified for compounds prepared and their binary mixtures with a standard polarized-light microscope (Wild, Heerbrugg, Germany), attached to a home made hot-stage. The temperature is measured by thermocouple connected to a Brookfield temperature controller, Derbyshire England.

Thin layer chromatography was performed with TLC sheets coated with silica gel (E. Merck); spots were detected by UV irradiation.

Infrared spectra (4000–400 cm⁻¹) were measured (Table 1) with a Perkin-Elmer B25 spectrophotometer, and ¹H NMR-spectra with Varian EM 350L.

3. Results and discussion

3.1. Confirmation of molecular structure

Infrared spectra, mass spectra, and elemental analyses for compounds investigated were consistent, within permissible limits, with the structures assigned. ¹H-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated.

3.2. Mesophase behavior

3.2.1. Simple molecules

Since the mesophase behavior of a liquid crystalline compound is dependent, in addition to other factors, upon the intermolecular attractions, in which molecular polarity plays a significant role, it has been shown [5] that, in a series of compounds, of nearly the same molecular shape, the dipole moment of any compound is dependent upon the nature of both the substituent and the mesogenic portion of the molecule to which this substituent is attached. A change in the extent of electronic interactions between the substituent, X, and the remainder of the molecule, alters the polarizability and resultant dipole moment of the molecule. In our case, electronic interactions between the substituents, X, and molecules of type I and II are expected to be different from that occurring with molecules of types III and IV. The phase transition temperatures and enthalpies of the prepared compounds $(I_{a-e}-IV_{a-e})$, as well as the entropies of the nematic-isotropic transitions, are collected in Table 2. The data in Table 2 revealed that, irrespective of either the position of the lateral methyl group, the polarity of the terminal substituent, *X*, or the relative positions of wing substituents, all compounds investigated were found to be monomorphic exhibiting the enantiotropic nematic phase as the only mesophase observed. To make the comparison of data in Table 1 clear, the substituent *X* attached to the mesomorphic compounds can be placed in the order of enhancing nematic phase stability of group I-IV compounds as:

Group I: $CN > CH_3O > NO_2 > CH_3 > Br$ Group II: $CN > CH_3O > NO_2 > CH_3 > Br$ Group III: $CN > CH_3O > NO_2 > CH_3 > Br$ Group IV: $CN > CH_3 > NO_2 > Br > CH_3O$



IIIa-e and IVa-e

Table 1
Infrared absorption spectra of represented compounds of Groups I_{a-e} -IV _{a-e} .

Comp. No.	Subst, X	V _{CH3} Asym.	V _{CH3} Sym.	ν _{C=0}	$\nu_{C=N}$	v_{C-0}	ν_{C-O}	$v_{\rm NO_2}$ (or $v_{\rm CN}$)
Ia	CH ₃ O	2930	2858	1730	1600	1465	1246	-
I _b	CH ₃	2931	2857	1727	1594	1473	1244	-
Ic	Br	2930	2858	1734	1589	1471	1250	-
Id	NO ₂	2930	2861	1732	1596	1476	1251	1535/1341
Ie	CN	2933	2863	1731	1594	1475	1254	2227
IIa	CH₃O	2928	2856	1734	1603	1470	1253	-
II _b	CH ₃	3929	2855	1729	1594	1474	1254	-
IIc	Br	2929	2860	1735	1586	1478	1252	-
\mathbf{II}_{d}	NO ₂	2931	2862	1731	1594	1484	1254	1524/1341
IIe	CN	2936	2862	1736	1590	1484	1255	2226
IIIa	CH₃O	2922	2851	1727	1603	1465	1242	-
III _b	CH₃	2921	2851	1728	1605	1467	1243	-
III _c	Br	2933	2862	1725	1602	1475	1258	-
III _d	NO ₂	2916	2851	1735	1608	1472	1241	1525/1345
III _e	CN	2936	2865	1724	1601	1490	1256	2224
IVa	CH₃O	2920	2849	1732	1606	1470	1260	-
IV _b	CH₃	2919	2847	1730	1604	1467	1253	-
IV c	Br	2932	2857	1736	1599	1468	1256	-
IV _d	NO ₂	2928	2850	1734	1626	1474	1248	1532/1344
IVe	CN	2940	2863	1731	1597	1474	1256	2223

That is, although wing substituents being exchanged between analogues of groups **I** and **III**, both groups obey the same order of nematic stability. Furthermore, while the lateral methyl group is oriented differently in groups **I** and **II** their nematic stability decreases in a parallel order. It can also be observed that, while the linear strong electron-withdrawing, CN group, is the best to enhance the nematic stability, the non-linear, also electronwithdrawing, NO₂ group occupies an intermediate order. The CH₃ and CH₃O groups nearly exchange their order in group **IV** compounds.

Alternatively, with respect to the effect of the terminal polar substituent, *X*, attached to any of the four isomeric groups, **I–IV**, the nematic stability was found to decrease in the order:

For	$X = CH_3O$	$III_a > I_a > II_a > IV_a$
	$X = CH_3$	$1212.6 204.1 187.6 151.2 \circ C$ $IV_b > I_b > II_b > III_b$
	X = Br	$I_{c}^{206.7} > IV_{c}^{180.8} > II_{c}^{168.4} > III_{c}^{138.9^{\circ}C}$
	$X = NO_2$	180.3 172.3 159.5 $133.0 \circ C$ $III_d > I_d > II_d > IV_d$
	X = CN	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
		222.5 216.8 213.2 209.0 °C

3.2.1.1. Lateral substitution and entropy change of transition, ΔS_{N-I} . The entropy of the nematic-isotropic transition was calculated for all members of the four series **I–IV**, and the results were appended to Table 2. It has been shown [13], for a related groups of compounds, that lateral substitution with the bulky methyl group is associated with lower values of ΔS_{N-I} than those of the corresponding laterally chloro-substituted analogues, independent of the length of the alkoxy chain. The decrease observed in ΔS_{N-I} was presumably in part a reflection of the increase in the biaxiality of the mesogenic group, which resulted in that the flexible terminal alkoxy chain being less anchored at its end, giving a resulting decrease in the conformational entropy [14]. Upon terminal substitution with different polar groups at either wing of the molecule, the behavior becomes more complex reflecting the variable extent of the strength of electronic interaction with the mesogenic core as a result of the change of the degree of conjugation. Thus, for the terminally 4-CH₃O substituted analogues in the four series, I_a -IV_a, the order of decrease in ΔS_{N-I} was mainly dependent on the nature of the mesogenic core, which definitely affects the lateral intermolecular interaction to a variable degree. That is, the order of decrease in ΔS_{N-I} was $III_a > I_a > IV_a$. Terminal substitution by the 4-CH₃ group is accompanied by an increase in ΔS_{N-I} in series I and IV,

Table 2

Phase transition temperatures (°C), enthalp	y of transition (ΔH , kJ/mole), and entropy	of clearing (ΔS_{N-I} , J/mole/K) for Group I_{a-e} -IV _{a-e}
---------------------------------------------	------------------------------------------------------	-----------------------------------------------------------------------------------

Comp. No.	X	T _{Cr-N}	$\Delta H_{\rm Cr-N}$	T _{N-I}	$\Delta H_{ m N-I}$	$\Delta S_{\rm N-I}$
Ia	CH ₃ O	118.5	45.2	204.1	1.66	3.48
Ib	CH ₃	94.0	45.0	180.8	1.78	3.92
I _c	Br	105.9	36.9	180.3	1.35	2.98
I _d	NO ₂	119.2	58.0	184.3	0.83	1.82
Ie	CN	136.9	37.2	209.0	1.37	2.84
IIIa	CH ₃ O	111.6	46.0	187.6	1.49	3.23
II _b	CH ₃	110.5	58.5	168.4	1.06	2.40
IIc	Br	117.3	44.7	159.5	1.39	3.21
\mathbf{II}_{d}	NO ₂	133.2	47.3	186.2	1.18	2.57
IIe	CN	150.7	48.6	213.2	2.45	5.04
IIIa	CH ₃ O	111.3	47.8	212.6	2.50	5.15
III _b	CH ₃	74.0	27.5	138.9	2.08	5.05
III _c	Br	90.5	28.3	133.0	0.57	1.40
III _d	NO ₂	115.5	50.9	199.2	0.95	2.01
IIIe	CN	121.8	56.2	222.5	0.80	1.61
IVa	CH ₃ O	84.9	27.1	151.2	0.86	2.03
IV _b	CH ₃	106.4	59.4	206.8	1.39	2.90
IVc	Br	105.7	56.9	172.3	0.89	2.00
IV _d	NO ₂	107.6	47.9	179.2	1.18	2.61
IV _e	CN	112.4	50.1	216.8	0.90	1.84

Cr, solid crystal; N, nematic; and I, isotropic.



Fig. 1. Dependence of the mesophase stability $(T_{C^{1/2}})$ on the polarizability anisotropy $(\Delta \alpha_X)$ of the substituent (*X*) attached to compounds of: (a) Group **I**, (b) Group **II**, (c) Group **III**, and (d) Group **IV**.

a significant decrease in series **II**, and slight decrease in series **III** where it decreases from $5.15 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ for **III**_b to $5.05 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ for **III**_a. Alternatively, when a comparison is made between $\Delta S_{\text{N-I}}$ values within members of any group of derivatives of the same core structure, $\Delta S_{\text{N-I}}$ was observed to decrease in an order which differ according to the nature of the terminal substituent as well as its position.

An explanation of the fact that the entropies do not correlate well with either the polarity of the substituent or with the clearing temperature, T_c , may be found in the conjugative interaction of the substituents (lateral or terminal) with the remainder of the molecule [1,15].

3.2.1.2. Clearing temperature and polarizability anisotropy of the C_{ar} -X bonds. The relationship between the stability of the mesophase, expressed as the clearing temperature, T_C , and the anisotropy of polarizability ($\Delta \alpha_X$) of bonds to small compact terminal substituent (C_{ar} -X) was studied by van der Veen [16]. The relation has the form:

$$T_{\rm C} \propto (\Delta \alpha_{\rm M} + \Delta \alpha_X)^2, \tag{1}$$

where $T_{\rm C}$ is measured in Kelvin. The term $\Delta \alpha_{\rm M}$ is the anisotropy of the polarizability for the whole molecular structure except the terminal substituent, *X*. Eq. (1) can be put in the form [7]:

$$\sqrt{T_{\rm C}} \propto (\Delta \alpha_{\rm M} + \Delta \alpha_X) = a \Delta \alpha_{\rm M} + a \Delta \alpha_X \tag{2}$$

where "*a*" is the proportionality constant. The values of $\Delta \alpha_X$ are given else where [17]. Thus, if $\sqrt{T_C}$ is plotted against $\Delta \alpha_X$ for any series of liquid crystalline compounds, a straight line is expected, the slope of which equals "*a*" and intercept equals " $a\Delta \alpha_M$ ". Consequently, $\Delta \alpha_M$ will be given by: $\Delta \alpha_M$ = intercept/slope.

The $\sqrt{T_C}$ values are plotted as a function of $\Delta \alpha_X$, for series **I–IV** in Fig. 1. As shown from Fig. 1, except for the data of Group **IV**, acceptable linear correlations were obtained for the other groups of compounds. Comparison of the slopes of the linear correlations in Fig. 1 revealed that, in a molecular core of type **I** or **II**, terminal substituent effect is more pronounced when the lateral methyl group is introduced in position 3 (II_{a-e}). This is evidenced from the higher slope of their linear correlations for group **II** compared with group **I**. The reverse holds good for molecular cores of groups **III** and **IV**. That is the slope for group **III** correlation, with lateral methyl group introduced into position 2, is higher than that or group **IV** (position 3).

3.2.2. Binary mixtures

It is already known that materials which exhibit its mesophase at room temperature and retain liquid crystalline character over a wide range of temperatures are preferred for practical applications. One way to achieve this property is to use eutectic mixtures of materials exhibiting liquid crystallinity in their pure state, or at least when the molecules in question resemble one another structurally. This is because under such condition, the mesophaseisotropic line is usually straight or slightly enhanced, and the temperature range of the mesophase is consequently greater for the low-melting eutectic mixture than either components of the mixture.

Based on the type of the two components of the binary mixture, we can formulate, using the compounds $I_{a-e}-IV_{a-e}$, two types of binary mixtures. The first is based on the difference in the position of the lateral CH₃-substituent, i.e., mixtures I/II and III/IV. The second type of binary mixtures to be investigated is based on the difference in the relative positions of the wing substituents (*X* and C₆H₁₃O), i.e., mixtures I/III and II/IV. Such mixtures aim to achieve a reasonable balance between improving mesomorphic properties and retaining advantageous physical properties of the laterally substituted components.

3.2.2.1. Binary mixtures of isomers bearing differently protruded methyl group I/II and III/IV. The binary phase diagrams for the 4-hexadecyloxyphenylazo (2-methylphenyl)-4substituted benzoates (I_{a-e}) with their isomeric derivatives, 4-hexadecyloxyphenylazo(3-methylphenyl)-4-substituted benzoates (II_{a-e}), are represented graphically in Fig. 2. The corresponding phase diagrams for the other two groups of isomers that bear the central methyl group with different protrusion, namely, 4-substituted phenylazo (2-methylphenyl)-4-hexadecyloxy benzoates (III_{a-e}) with their isomeric derivatives, 4-substituted phenylazo-(3-methylphenyl)-4-hexadecyloxybenzoates (**IV**_{a-e}), are represented graphically in Fig. 3. As can be seen from Figs. 2 and 3, irrespective of the terminal substituent attached to either side of the molecule or the position of the central methyl group, linear nematic behaviors were observed in all systems investigated, indicating that the addition of one component to the other does not disturb the nematic arrangements exhibited by both molecules. Such behavior necessitates the back-to-face arrangements of molecules that do not allow steric methyl-methyl interaction that would have lead to a negative deviation from the linear behavior. Figs. 2 and 3 also indicate that all systems exhibit eutectic composition, with melting points as low as 60 °C for the binary system III_b/IV_b, Fig. 3b.

The composition, phase transition temperatures, and the nematic ranges ($\Delta T = T_{N-I} - T_{Cr-N}$) of the eutectic mixtures, as deduced from Figs. 2 and 3, are collected in Table 3, from which it can be seen that, according to the substituent *X*, the mesophase ranges ($\Delta T = T_m - T_{N-I}$) for the two systems investigated at their eutectic compositions decreases in the order



Fig. 2. Binary phase diagrams of the binary systems (I/II) with various terminal substituents. (a) X = CH₃O, (b) X = CH₃O, (c) X = Br, (d) X = NO₂, and (e) X = CN.



Fig. 3. Binary phase diagrams of the binary systems (III/IV) with various terminal substituents. (a) X = CH₃O, (b) X = CH₃O, (c) X = Br, (d) X = NO₂, and (e) X = CN.



Fig. 4. Binary phase diagrams of the binary systems (I/III) with various terminal substituents. (a) X = CH₃O, (b) X = CH₃O, (c) X = Br, (d) X = NO₂, and (e) X = CN.



Fig. 5. Binary phase diagrams of the binary systems (II/IV) with various terminal substituents. (a) X = CH₃O, (b) X = CH₃O, (b) X = Br, (d) X = NO₂, and (e) X = CN.

Table 3

Composition, melting temperatures (T_m , °C), clearing temperatures (T_{N-1} , °C), nematic ranges ($\Delta T = T_{N-1} - T_m$, °C), and the calculated T_E values of the eutectic binary mixtures, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{II}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}$, $\mathbf{I}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{II}_{a-e}/\mathbf{$

Mixture	Subst. X	Composition (%)	<i>T</i> _m (°C)	<i>T</i> _E (°C)	<i>T</i> _{N−I} (°C)	$\Delta T(^{\circ}C)$
I _a /II _a	CH ₃ O	65.3% II a	90.0	95.7	215.5	125.5
$I_{\rm b}/II_{\rm b}$	CH ₃	41.3% II _b	84.0	81.3	182.0	98.0
I_c/II_c	Br	50.5% II c	90.1	84.4	172.0	82.0
I_d/II_d	NO ₂	69.3% II _d	114.0	101.6	179.5	65.5
I _e /II _e	CN	50.0% II _e	108.0	112.4	209.0	101.0
III _a /IV _a	CH ₃ O	76.7% IV a	70.0	74.7	164.5	96.5
III_b/IV_b	CH_3	24.0% IV b	60.0	64.3	152.0	92.0
III _c /IV _c	Br	40.0% IV _c	68.0	71.7	143.0	75.0
III_d/IV_d	NO ₂	65.3% IV d	88.0	91.0	184.0	96.0
III _e /IV _e	CN	75.3% IV e	84.0	92.0	219.2	135.2
I _a /III _a	CH ₃ O	73.3% III a	90.0	84.5	209.0	119.0
$I_{\rm b}/III_{\rm b}$	CH_3	76.0% III _b	61.0	61.6	158.0	97.0
I _c /III _c	Br	71.3% III _c	65.5	69.4	139.0	73.5
I_d/III_d	NO ₂	43.0% III _d	88.0	95.7	182.0	94.0
I _e /III _e	CN	57.7% III _e	106.8	106.9	216.8	110.0
II _a /IV _a	CH ₃ O	72.7% IV a	68.0	72.8	160.0	92.0
II_b/IV_b	CH ₃	58.7% IV b	86.0	92.9	190.0	104.0
II _c /IV _c	Br	41.3% IV c	78.0	88.0	170.0	92.0
II_d/IV_d	NO ₂	75.3% IV _d	66.0	75.4	182.0	116.0
II_e/IV_e	CN	76.1% IV e	94.2	105.8	215.0	120.8

Mixture I/II: $CH_3O > CN > CH_3 > Br > NO_2$. Mixture III/IV: $CN > NO_2 > CH_3O > CH_3 > Br$.

Whereas, the nematic stability, according to the substituent *X*, for the eutectic compositions for these two groups of binary mixtures decreases in the order:

Mixture I/II: $CH_3O > CN > CH_3 > NO_2 > Br$. Mixture III/IV: $NO_2 > CH_3O > CN > CH_3 > Br$.

3.2.2.2. Binary mixtures of isomers with exchanged terminal substituents, I/III and II/IV. The binary phase diagrams for the 4-hexadecyloxyphenylazo (2-methylphenyl)-4-substituted benzoates (I_{a-e}) with their isomeric derivatives, 4-substituted phenylazo-(2-methylphenyl)-4-hexadecyloxy benzoates (III_{a-e}), are represented graphically in Fig. 4. The binary phase diagrams for the corresponding two groups of isomers that bear the central methyl group in position-3, namely, 4-hexadecyloxyphenylazo-(3-methylphenyl)-4-substituted benzoates (II_{a-e}) with their isomeric derivatives, 4-substituted phenylazo-(3-methylphenyl)-4hexadecyloxy benzoates (IV_{a-e}) , are represented graphically in Fig. 5. As can be seen from Figs. 4 and 5, irrespective of the nature of the lateral substituent, X, the introduction of such substituent on either wings of the molecule, namely, I compared to III or II compared to IV, do not alter the type of molecular arrangement within the nematic mesophase to such an extent that all binary mixtures behaved ideally. With respect to their effect on the nematic range and stability at the eutectic compositions, ΔT_{N-I} decreases in the order:

Mixture I/III: $CH_3O > CH_3 > NO_2 > CN > Br$. Mixture II/IV: $NO_2 > CH_3 > CH_3O > Br > CN$.

And the nematic range decreases in the order:

Mixture I/III: $CH_3O > NO_2 > CH_3 > CN > Br$. Mixture II/IV: $CH_3 > NO_2 > Br > CH_3O > CN$.

3.2.3. Eutectic behavior of mixtures

Predicting the crystal-mesophase transition temperatures, $T_{\rm m}$, of a mixture is quite a bit less straight forward. The solubility of compounds in a mixture, which behaves as a thermodynamically

ideal system, follows the vant't Hoff relation, which is conveniently recast into the Schroeder-van Laar equation [18–20]:

$$\ln \chi_i = \left(\frac{\Delta H_i}{R}\right) \left(\frac{1}{T_E}\right) - \left(\frac{1}{T_i}\right) \tag{3}$$

in which the melting point (T_E) of the eutectic mixture is related to the mole fraction (χ_i), crystal-mesophase transition temperature (T_i), and the molar enthalpy of fusion (ΔH_i) of component "*i*" in a mixture. *R* is the gas constant. Knowing the values of χ_i , T_i , and ΔH_i , T_E could be calculated, using Eq. (3), and the calculated T_E values were included to Table 3. The difference between the measured, T_m , and calculated, T_E , eutectic melting temperatures can be taken as a measure of deviation from ideal solid behavior. Coincidence or deviations are dependent on differences in the core structures of both components of the mixture, orientation of the lateral methyl group in both components, and/or the polarity of the terminal group, *X*. Deviations from ideal behavior are sufficiently common and large to make this approach unreliable [21].

4. Conclusions

Four homologous series ($I_{a-e}-IV_{a-e}$) of the laterally methyl substituted derivatives were prepared, the first two groups (I and II) have the molecular formula 4-(4'-hexyloxyphenylazo)-2-(or 3-)methylphenyl-4"-substituted benzoates, while the other two groups, III and IV, are their respective isomers in which the last two groups (II and IV) have the molecular formula 4-(4'-substituted phenylazo)-2-(or 3-) methylphenyl-4"-hexyloxy benzoates. All compounds prepared were investigated for their mesophase behavior in mixed states.

Combining the added properties of the lateral CH_3 and the terminal polar, *X*, substituents, significant changes were observed in the mesomorphic behavior of the resulted derivatives and their binary mixtures. Varying extents of mesomeric interactions between the central CH_3 group (in position 2 or 3) as well as the terminal polar substituent, *X*, with the ester C=O group, which definitely depend on the polarity and position of *X*, is reflected on the resultant dipole moments, and consequently on their mesomorphic properties. The study revealed that all compounds prepared, irrespective of the position of the three substituents (CH_3 , $C_6H_{13}O$, or *X*), are enantiotropically nematogenic. Two types of binary phase diagrams, namely, **I**/**II** and **III**/**IV**, were constructed for all possible binary mixtures made from any two isomers of the same skeletal structure except the orientation of the central lateral CH₃ substituent. The other two groups of diagrams investigated were made from isomers of similar molecular core but of the terminal ($C_6H_{13}O$ and X) are being exchanged, i.e., the two binary systems **I**/**III** and **II**/**IV**.

The binary mixtures investigated were found to exhibit, in all cases, eutectic compositions with relatively low melting points that also differ according to the polarity and relative position of the terminal polar group, *X*, as well as the orientation of the central methyl group attached to the two components of the mixture. Linear nematic behavior was observed in all mixtures investigated as indicated from the linear T_{N-1} – composition dependencies.

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