Effect of exchange of terminal substituents on the mesophase behaviour of some azo/ester compounds

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Six homologous series of 4-(4′-alkoxy phenylazo) phenyl 4″-substituted benzoates (I\textsubscript{na,\textit{d}}) were prepared in which, within each homologous series, the length of the terminal alkoxy chain varies between 6, 8, 10, and 12 carbons, while the other terminal substituent, X, is a polar group that alternatively changed from CH\textsubscript{3}O, CH\textsubscript{3}, H, Br, NO\textsubscript{2} and CN. Compounds prepared were characterised by spectroscopic methods, and their mesophase behaviour investigated by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). The results were discussed in terms of mesomeric and polarisability effects. In each group of compounds, bearing the same alkoxy substituent, the nematic-to-isotropic transition temperatures (T\textsubscript{c}) were successfully correlated with the polarisability anisotropy of bonds to the substituent X. A comparative study was made between the investigated compounds and their previously prepared isomers, namely, 4-(4′-substituted phenylazo) phenyl 4″-alkoxybenzoates (II\textsubscript{na,\textit{d}}) in which the two terminal (alkoxy- and X) groups are exchanged.

**Keywords:** phenylazo phenyl benzoates; mesophase behaviour; exchange of terminal groups; polarisability anisotropy

1. Introduction

In calametic liquid crystals both permanent dipoles and polarisable moieties are required, whereby the thermal stability of the mesophase formed depends, to a great extent, on subtle structural, steric and electronic effects within the central and terminal groups. Attempts to correlate the mesophase stability with molecular structure are based on considerations of the nature and magnitude of the intermolecular forces that favour the lateral association of their rod-shaped molecules. However, intermolecular forces due dipole–dipole interactions have shown [1–7] not to be the only factors important in promoting mesophase stability. Linking groups that maintain rigidity and linearity of the molecule are satisfactory in this respect. The ester (COO) group is one of the most commonly used linking units since it is relatively thermally stable. In addition, mutual conjugation within the ester moiety and the rings leads to some double bond character, and the mesophase becomes more persistent when the mutual conjugation between the substituent and the ester carbonyl (or oxygen) is increased. [8–12] Azobenzene group represents very comfortable fragments to design and synthesise new structures, giving stable mesophases often with very interesting polymorphism. [13–17] Liquid crystal materials bearing azo/ester central linkages and middle and terminal phenyl rings substituted with groups of different polarity as well as n-alkoxy group on the other end of the molecule were reported. [18–27]

In previous work [28] in this laboratory, the effect of compact terminal substituent (X), as well as the terminal alkoxy (RO-) group, of varying chain length, on the mesophase behaviour of compounds of the type 4-(4′-substituted phenylazo) phenyl 4″-alkoxybenzoates (II\textsubscript{na,\textit{d}}) was studied. In that work, [28] it was observed that the stability of the mesophase is augmented by an increase in the polarity and/or polarisability of the mesogenic part of the molecule, which is definitely affected by the polarity of the substituent, and its position, which would accordingly affect the polarity of the whole molecular structure by the way the polar substituents electronically interact with the remainder of the molecule. Thus, in compounds of the type II, [28] for the electron-withdrawing cyano or nitro groups, mesomeric interaction between the alkoxy oxygen and the ester carbonyl, on one side of the molecule, is augmented by the conjugative interaction between the ester oxygen and the cyano (or nitro) group via the phenylazo benzene group, on the other side of the molecule. This should increase the polarity of the mesogenic portion as a whole and consequently stabilises the mesophase. Such increased polarisability, to cover almost the whole mesogenic portion of the molecule, increases the lateral interaction between adjacent molecules and leads to smectic phase formation; this was found to be the case. [28] Conversely, there are opposite electronic interactions on both sides of the molecule in the case of the methoxy or methyl analogues. The latter derivatives are expected to possess lower dipolar character and consequently...
lead to nematogenic derivatives possessing lower lateral association and accordingly lower clearing temperatures,\cite{28} i.e. transitions to the isotropic phase.

As expected, exchange of the two terminal substituents (RO and X) in a compound of type II, results in an isomer, I, would react mesomerically in a different way and consequently possess a different mesophase behaviour. The goal of the present work is to extend the investigation to isomeric compounds of the type 4-(4′-alkoxy phenylazo) phenyl 4″-substituted benzoates (I\(_{n_a-f}\)), in which the two terminal (RO and X) groups in the previously investigated compounds \cite{28} exchanges their positions. These new compounds, I\(_{n_a-f}\), will be prepared, chemically characterised, investigated for their mesophase behaviour, and compared with their previously prepared positional isomers (II\(_{n_a-f}\)).

![Chemical structure of I\(_{n_a-f}\) and II\(_{n_a-f}\)](image)

2. Experiment

Chemicals were of very pure grades and purchased from the following companies: Fluka, Buchs, Switzerland; MP Biomedicals, Inc., Illkirch, France; BDH, Poole, England; Aldrich, Wisconsin, USA; and E. Merck, Darmstadt, Germany.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded as KBr pellets, using a Perkin-Elmer B25 spectrophotometer. \(^1\)H nuclear magnetic resonance (\(^1\)H NMR) spectra were obtained with a Varian EM 350 L in CDCl\(_3\) with tetramethyl silane (TMS), as the internal standard. Mass spectra were obtained on GCMS-QP1000EX mass spectrometer (Shimadzu, Japan). Purity of all compounds was confirmed via thin-layer chromatography and elemental analysis.

Temperatures of phase transitions and their enthalpies were determined using a differential scanning calorimeter, PL-DSC (Polymer Laboratories, London, England). The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga et al.\cite{29} DSC measurements were carried out for small samples (2–3 mg) placed in sealed aluminium pans. All the thermograms have been achieved at a heating rate of 10°C/min in an inert atmosphere of nitrogen gas (20 ml/min).

Transition temperatures were checked and type of mesophase identified for all compounds prepared with a standard polarised optical microscope (POM) (Wild, Germany) attached to a homemade hot-stage. The textures of the mesophases were checked by a miscibility method using standard compounds under the POM.

The purity of samples prepared were checked with thin-layer chromatography using TLC-sheets coated with silica gel and CH\(_2\)Cl\(_2\)/CH\(_3\)OH (9:1) as eluent, whereby only one spot was detected by a UV lamp.

2.1 Preparation of materials

Investigated compounds (I\(_{n_a-f}\)) were prepared according to the following scheme:

![Chemical reaction scheme](image)
2.1.1 Preparation of 4-alkoxy aniline hydrochlorides

4-Alkoxylaniline was first prepared from 4-hydroxyaniline (0.1 mole) and the appropriate amount of 1-bromoalkane (0.12 mole); the anilines were then hydrolysed, to the corresponding aniline hydrochlorides, by refluxing with concentrated hydrochloric acid for 24 hr, and the alkoxylaniline hydrochlorides were used as such in the successive steps.

2.1.2 Preparation of 4-alkoxy phenyl azo phenols (An)

The 4-alkoxyaniline hydrochloride (0.01 mole) was dissolved in 3 ml hot concentrated hydrochloric acid and cooled in ice-salt bath to 0°C. To the resulting solution, a cold aqueous solution of sodium nitrite (0.03 mole) was added dropwise with stirring. During the addition, the temperatures did not exceed 2°C. After complete addition, the cold mixture was added dropwise to an ice-cold aqueous solution of phenol (0.01 mole) in sodium hydroxide (0.03 mole). The mixture was further stirred at 0°C for 1 hr then acidified with dilute hydrochloric acid. The solid separated was filtered off and crystallised twice from ethanol. The products were TLC pure and gave melting points that agreed with those reported in literature.

2.1.3 Preparation of 4-(4'-alkoxy phenylazo) phenyl 4'-substituted benzoates (In)

Molar equivalents of 4-alkoxy phenylazo phenol (An) and 4-substituted benzoic acid (0.001 mol each) were dissolved in 25 ml of dry methylene chloride. To the resulting mixture, dicyclohexyl carbodiimide (DCC, 0.002 mole) and few crystals of 4-(dimethylaminomino) pyridine (DMAP), as a catalyst, were added and the mixture stirred at room temperature for 3 days. The solid separated was filtered off and the solution evaporated; the residue obtained was crystallised twice from ethanol. The purity of the products obtained was checked by TLC using CH₂CL₂/CH₃OH (9:1) as eluent; one spot was observed.

Results of elemental analysis of all the compounds of the synthesised series In were found to be satisfactory (Supplementary data). Since almost identical infrared and ¹H NMR spectra were observed for all the members of the six homologous series (In₁–In₆), FT-IR and ¹H NMR spectral data of the n-octyloxy derivatives (I₈₀⁻), as examples, are given below:

For I₈₀, FT-IR (KBr, υₜ₇₈₇ cm⁻¹): 3068 (C–H aromatic) 2942, 2864 (alkyl group), 1584 (–C=C– aromatic), 1729, 1254 (–COO– group), 1605 (–N=O– group), 838 (p-sub. benzene rings).

¹H NMR (300 MHz, CDCl₃) δ ppm: 0.87–0.91 (t, 3H, –CH₃), 1.25–1.87 (m, 12H, 6 × –CH₂–), 4.03–4.09 (t, 2H, –OCH₂–), 3.85 (s, 3H, Ar–OCH₃), 6.97–7.84, 7.36–8.01, 6.92–8.05 (m, 12 H, p-subst. benzene rings).

For I₈₁, FT-IR (KBr, υₜ₇₈₇ cm⁻¹): 3059 (C–H aromatic) 2918, 2848 (alkyl group), 1586 (–C=C– aromatic), 1743, 1251 (–COO– group), 1601 (–N=O– group), 831 (p-sub. benzene rings).

¹H NMR (300 MHz, CDCl₃) δ ppm: 0.87–0.91 (t, 3H, –CH₃), 1.25–1.87 (m, 12H, 6 × –CH₂–), 2.35 (s, 3H, Ar–CH₃), 4.03–4.09 (t, 2H, –OCH₂–), 6.97–7.84, 7.36–8.01, 7.21–8.04 (m, 12 H, p-sub. benzene rings).

For I₈₂, FT-IR (KBr, υₜ₇₈₇ cm⁻¹): 3061 (C–H aromatic) 2918, 2850 (alkyl group), 1584 (–C=C– aromatic), 1741, 1253 (–COO– group), 1602 (–N=O– group), 839 (p-sub. benzene rings).

¹H NMR (300 MHz, CDCl₃) δ ppm: 0.87–0.91 (t, 3H, –CH₃), 1.25–1.87 (m, 12H, 6 × –CH₂–), 4.03–4.09 (t, 2H, –OCH₂–), 6.97–7.84, 7.36–8.01, 7.41–8.15 (m, 12 H, p-sub. benzene rings).

For I₈₃, FT-IR (KBr, υₜ₇₈₇ cm⁻¹): 3045 (C–H aromatic) 2919, 2850 (alkyl group), 1584 (–C=C– aromatic), 1740, 1251 (–COO– group), 1630 (–N=O– group), 1055 (C–Br aromatic), 841 (p-sub. benzene rings).

¹H NMR (300 MHz, CDCl₃) δ ppm: 0.87–0.91 (t, 3H, –CH₃), 1.25–1.87 (m, 12H, 6 × –CH₂–), 4.03–4.09 (t, 2H, –OCH₂–), 6.97–7.84, 7.36–8.01, 7.61–8.04 (m, 12 H, p-sub. benzene rings).

For I₈₄, FT-IR (KBr, υₜ₇₈₇ cm⁻¹): 3068 (C–H aromatic) 2919, 2851 (alkyl group), 1584 (–C=C– aromatic), 1741, 1253 (–COO– group), 1601 (–N=O– group), 1533, 1347 (Ar–NO₂), 838 (p-sub. benzene rings).

¹H NMR (300 MHz, CDCl₃) δ ppm: 0.87–0.91 (t, 3H, –CH₃), 1.25–1.87 (m, 12H, 6 × –CH₂–), 4.03–4.09 (t, 2H, –OCH₂–), 3.85, 6.97–7.84, 7.36–8.01, 8.34–8.41 (m, 12 H, p-sub. benzene rings).

For I₈₅, FT-IR (KBr, υₜ₇₈₇ cm⁻¹): 3057 (C–H aromatic) 2921, 2851 (alkyl group), 1587 (–C=C– aromatic), 1736, 1246 (–COO– group), 1601 (–N=O– group), 2232 (–CN), 838 (p-sub. benzene rings).

¹H NMR (300 MHz, CDCl₃) δ ppm: 0.87–0.91 (t, 3H, –CH₃), 1.25–1.87 (m, 12H, 6 × –CH₂–), 4.03–4.09 (t, 2H, –OCH₂–), 6.97–7.84, 7.36–8.01, 7.66–8.34 (m, 12 H, p-sub. benzene rings).
3. Results and discussion

3.1 Confirmation of molecular structure
The molecular structures of the newly prepared azol ester homologues (Im\textsubscript{a-f}) were confirmed via elemental analyses, FT-IR, NMR and mass spectra. Elemental analyses were in agreement, within permissible limits, with the proposed formulae. \textsuperscript{1}H NMR data showed expected integrated aliphatic-aromatic ratios in all compounds investigated. Mass spectra indicated exact molecular masses for the whole molecular structures and expected fragmentation.

The nearly identical infrared absorption spectra observed for the four series previously investigated \[28\] (II\textsubscript{6a-f} - II\textsubscript{12a-f}) revealed that neither the length of the alkoxy chain, C6-C12, in any of the homologous series, nor the substituent X in any group of derivatives bearing the same alkoxy group has a significant effect on the position of infrared absorption bands; e.g. \nu\textsubscript{C=O} varies between 1720 cm\textsuperscript{-1} for the CH\textsubscript{3}O-substituted analogue, II\textsubscript{8a}, and 1726 cm\textsuperscript{-1} for its nitro-analogue. This is expected, since the polar substituent (X) is attached to the ester oxygen group via a phenylazo phenyl moiety. Conversely, in the present series of compounds (I\textsubscript{6a-f}-I\textsubscript{12a-f}), there are relatively a significant variation in the C=O absorption bands since in this case the polar substituent (X) is directly attached to position 4 with respect to the carbonyl ester group.

3.2 Mesophase behaviour of compounds investigated
Since the mesophase stability of a liquid crystalline compound depends mainly upon intermolecular attractions in which molecular polarity plays a significant role, it has been shown \[2\] that within one series of compounds, e.g. I\textsubscript{6a-f}, the dipole moments of its individuals are determined by the nature of the substituents. A change in the extent of conjugation alters the polarisability and resultant dipole moment of the molecule. It has also been shown \[4\] that the dipole moments of all the members of a homologous series are virtually identical, irrespective of the length of the alkoxy chain. This result is supported by the fact that the alkoxy groups have similar polarity regardless of their length and at the same time do not affect the degree of conjugative interaction between the alkoxy oxygen and the ester carbonyl, as is confirmed by infrared measurements. Transition temperatures and enthalpies measured by DSC, and phases identified by POM, for the newly prepared compounds Im\textsubscript{a-f} are summarised in Table 1. It is obvious that the enthalpy values of the various transitions agree well with the existing related literature values.[31] Corresponding data for compounds Im\textsubscript{a-f} are given elsewhere.[28] Mesophase behaviours of the newly prepared series, Im\textsubscript{a-f}, as a function of alkoxy chain length, are depicted in Figure 1. The effect of increasing alkoxy chain length on the mesophase stability (T\textsubscript{C}) of compounds of series I and II (for reason of comparison) are plotted collectively in Figure 2. These plots show that, irrespective of the substituent X, the mesophase-to-isotropic transition temperatures (T\textsubscript{C}) decrease regularly with increasing the alkoxy chain length. The pattern of behaviour is in accordance with that shown by Gray \[8\] and Imrie and Taylor,[32] in which the nematic-to-isotropic transition temperatures fall with increasing alkoxy chain length, and if the series also exhibits smectic properties, then the smectic-nematic transition temperatures will be found to rise steeply at first and then more gradually as the alkoxy chain lengthens (see Figure 1). The smectic-nematic curves become coincident with the falling nematic-isotropic curve before the former has reached its maximum. The thermal stability of a smectic-mesophase, which at higher temperature is replaced by a nematic one, is determined by the intermolecular attraction which laterally operates between the sides of molecules. Thus, in the cyano (or nitro) homologues in compounds Im or Im, the interactions between the alkoxy oxygen and the phenylazo group, in one side of the molecule, is augmented by the inductive electron-withdrawing power (-I) of the cyano (or nitro) group, on the other side of molecule. Similarly, in compounds I the mesomorphic interaction between the alkoxy oxygen and the ester carbonyl, on one side of the molecule, is again augmented by the conjugal interaction between the ester oxygen and the CN (or NO\textsubscript{2}) group via the phenylazo benzene group, on the other side of the molecule of group I (i.e. Im\textsubscript{a-f} or Im\textsubscript{a-f}). In both the cases, this should increase the polarity of the mesogenic portion as a whole and consequently stabilises the mesophase (high T\textsubscript{C} values). This inference is in accordance with the experimental results that the cyano and nitro analogues (in both series I and II) have the highest clearing (T\textsubscript{C}) temperatures.
Conversely, there are opposing effects on each side of either molecules I or II of the methoxy (I_6 and II_6) and methyl (I_6 and II_6) analogues. Accordingly, they are expected to possess lower dipolar character that would lead to derivatives with lower \( T_C \) values.

Conjugative interactions in the cyano substituted derivatives I_6 and II_6.

| Compound | n | \( X \) | \( T_{C-A} \) | \( T_{C-N} \) | \( T_{A-N} \) | \( T_{A-I} \) | \( T_{N-I} \) |
|----------|---|-------|-------------|-------------|-------------|-------------|-------------|
| I_{6a}   | 6 | OCH₃  | –           | 107 (44.11) | –           | –           | 257 (2.21)  |
| I_{6b}   |   | CH₃   | –           | 130 (38.18) | –           | –           | 215 (1.70)  |
| I_{6c}   |   | H     | –           | 122 (34.41) | –           | –           | 161 (2.57)  |
| I_{6d}   |   | Br    | 97 (25.91)  | 101 (0.69)  | –           | –           | 238 (2.03)  |
| I_{6e}   |   | NO₂   | –           | 121 (41.61) | –           | –           | 276 (3.21)  |
| I_{6f}   |   | CN    | –           | 137 (18.01) | –           | –           | 271 (2.82)  |
| I_{8a}   | 8 | OCH₃  | –           | 103 (53.04) | –           | –           | 222 (2.30)  |
| I_{8b}   |   | CH₃   | –           | 138 (38.81) | –           | –           | 195 (1.55)  |
| I_{8c}   |   | H     | –           | 124 (37.53) | –           | –           | 152 (2.23)  |
| I_{8d}   |   | Br    | 138 (30.18) | –           | 152 (8.56)  | –           | 213 (1.86)  |
| I_{8e}   |   | NO₂   | 122 (46.40) | –           | 212 (4.46)  | –           | 252 (1.66)  |
| I_{8f}   |   | CN    | 135 (40.58) | –           | 149 (3.86)  | –           | 249 (1.13)  |
| I_{10a}  | 10| OCH₃  | –           | 104 (51.63) | –           | –           | 209 (1.85)  |
| I_{10b}  |   | CH₃   | –           | 118 (38.85) | –           | –           | 180 (1.48)  |
| I_{10c}  |   | H     | –           | 112 (36.68) | –           | –           | 143 (1.09)  |
| I_{10d}  |   | Br    | 147 (55.06) | –           | 173 (3.43)  | –           | 191 (1.98)  |
| I_{10e}  |   | NO₂   | 115 (45.01) | –           | 227 (3.21)  | –           | 242 (1.15)  |
| I_{10f}  |   | CN    | 110 (38.59) | –           | 220 (2.84)  | –           | 232 (1.01)  |
| I_{12a}  | 12| OCH₃  | –           | 108 (60.08) | –           | –           | 207 (1.39)  |
| I_{12b}  |   | CH₃   | –           | 114 (42.80) | –           | –           | 177 (1.30)  |
| I_{12c}  |   | H     | –           | 115 (39.49) | –           | –           | 140 (1.16)  |
| I_{12d}  |   | Br    | 146 (55.78) | –           | –           | 184 (4.45)  | –           |
| I_{12e}  |   | NO₂   | 112 (62.42)| –           | –           | 234 (6.00)  | –           |
| I_{12f}  |   | CN    | 113 (53.92)| –           | –           | 230 (4.19)  | –           |

Notes: Cr-A denotes transition from solid to the SmA phase.
Cr-N denotes transition from solid to the N phase.
A-N denotes transition from SmA to the N phase.
A-I denotes transition from SmA to the isotropic phase.
N-I denotes transition from Nematic to the isotropic phase.
Figure 1. Dependence of transition temperatures of $\text{In}_a-f$ on the alkoxy chain length ($n$).

Conjugative interactions in the methoxy substituted derivatives $\text{In}_a$ and $\text{II}n_a$. 

$\text{In}_a$ 

$\text{II}n_a$
As can be seen, in both the series of compounds (I and II) the nitro and cyano derivatives possess the highest $T_C$ values followed by the bromo analogues, the methoxy, the methyl and finally the unsubstituted.

Investigation of the effect of exchange of terminal substituents (RO and X) on the mesophase behaviour of the corresponding isomeric pairs (Figure 2) revealed that it depends on the polar compact substituent. Thus, for the electron-donating group (CH$_3$O and CH$_3$), the unsubstituted (X=H) and the halogen-substituted analogue, compounds II$_{a-d}$ are of higher mesophase stability than their corresponding isomers, I$_{a-d}$. With respect to the nitro-substituted I$_e$ and II$_e$, reversed behaviour is observed, i.e. I$_e$ is of higher stability. As for the strong electron-withdrawing substituted isomers I$_f$ and II$_f$, the stability of the mesophase depends on the length of the alkoxy chain ($n$). That is, for $n = 6$ compound I$_6$ is of higher stability than II$_6$, while the reverse holds true for higher homologues, i.e. II$_n$ > I$_n$.

### 3.3 Clearing temperatures and polarisability anisotropy of the $C_{ar}$-X

The relationship derived by van der Veen [33] between the stability of the mesophase, expressed as the clearing temperature, $T_C$, and the anisotropy of polarisability ($\Delta \alpha_X$) of bonds to small compact terminal substituent ($C_{ar}$-X), has the form:

$$T_C = \alpha (\Delta \alpha_M + \Delta \alpha_X)^2$$

where $T_C$ is measured in Kelvin. Equation (1) can be put in the form [3]:

$$T_C^{1/2} = a(\Delta \alpha_M + \Delta \alpha_X) = a\Delta \alpha_M + a\Delta \alpha_X$$

The term $\Delta \alpha_M$ is the polarisability anisotropy of all the molecular structure except the terminal substituent, X, and 'a' is the proportionality constant. Thus, if $T_C^{1/2}$ of any of our investigated compounds, bearing one and the same alkoxy group, $n$, but of varying X, is plotted against $\Delta \alpha_X$, a straight line is expected with a slope 'a'.
and intercept equals \( a \Delta \alpha_M \). Where \( a \Delta \alpha_M = \text{intercept/slope} \) is the polarisability anisotropy of the whole molecular structure except the substituent X. The \( T_c^{1/2} \) values were plotted, individually, for each series bearing the alkoxy group (n), as a function of the polarisability anisotropy \( \Delta \alpha_C \), as calculated previously,\(^{[3]} \) and the plots are depicted in Figure 3. It should be mentioned here that all the compounds exhibit the nematic phase, except for \( \text{II}_2\text{a-f}, \text{II}_2\text{e} \) and \( \text{II}_2\text{f} \) which are purely smectogenic. Their values were represented in Figure 3 as solid circles. The slopes and intercepts were calculated for each regression line, in Figure 3, by the method of least squares, from which \( \Delta \alpha_M \) could be calculated for the four series of compounds; the results are given in Table 2. As can be seen from Figure 3, fairly linear dependencies were observed.

Comparison of \( \Delta \alpha_M \) values as a function of the number of carbon atoms in the alkoxy chain in both the series of compounds (I and II) revealed that the polarisability anisotropy of the molecule \( \text{I}_{n\text{a-f}} \), excluding the substituent X, increases as the alkoxy chain (n) is lengthened (see Table 2). This trend is found to be opposite to that observed for series II \( \text{[28]} \) in which \( \Delta \alpha_M \) decreases with \( n \); the \( \Delta \alpha_M \) values are appended to Table 2. The former trend reflects an increase in the molecular rigidity and polarity of the molecule, while in the latter, \( \text{II}_{n\text{a-f}}, \) both properties were found to decrease as a result of increasing the alkane character.

The nature and length of the central mesogenic group are also of great importance. This can be investigated by comparing compounds, \( \text{I}_{n\text{a-f}}, \) with the correspondingly substituted 4-aryl-4’-alkyloxybenzoates, \( \text{III}_{[4]} \) and 1,4-phenylene-bis-4’-substituted benzoates, \( \text{IV}_{[34]} \) with respect to the crystal–mesophase (\( T_m \)) and mesophase–isotropic (\( T_C \)) transition temperatures, as well as the mesomorphic ranges, \( \Delta T = T_C - T_m \).

![Figure 3. Effect of the polarisability anisotropy, \( \Delta \alpha_C \), of the \( \text{C}_n\text{-X} \) bonds on the clearing temperature (\( T_C \)) of compounds \( \text{I}_{n\text{a-f}} \). Symbol ‘•’ denotes SmA to isotropic.](image)

| Series | \( n \) | Slope \( (\times 10^{23}) \) | Intercept \( (\text{K}^1) \) | \( \Delta \alpha_M \times 10^{23} \) | \( \Delta \alpha_M \times 10^{23} \) |
|--------|--------|------------------|----------------|------------------|------------------|
| \( \text{I}_{6\text{a-f}} \) | 6 | 5.17 | 20.93 | 4.05 | 3.96 |
| \( \text{I}_{8\text{a-f}} \) | 8 | 4.59 | 20.64 | 4.50 | 3.79 |
| \( \text{I}_{10\text{a-f}} \) | 10 | 4.40 | 20.34 | 4.62 | 3.63 |
| \( \text{I}_{12\text{a-f}} \) | 12 | 4.36 | 20.26 | 4.65 | 3.48 |

Corresponding analogues in the three groups of compounds (I, III and IV) differ from each other in the mesogenic segment of the molecule, but they do contain the same terminal substituents (X and RO). The study revealed that the introduction of a phenylazo moiety into the phenyl benzoate molecule \( [4] \) in III to form I results in an increase of the intermolecular forces and consequently of the stability of the solid and mesophase; i.e. results in an increase in the melting and clearing temperatures. Furthermore, while the methoxy and methyl-substituted analogues of III showed monotropic mesophases, the corresponding analogues in series I showed enantiotropic mesophases with high clearing temperatures. On the other hand, replacement of the ester group in IV \( [35] \)
by an azo linkage in I has led to a decrease in $T_m$ and an increase in $T_C$; i.e. compounds I have greater mesomorphic ranges than those of the corresponding analogues in series IV. This conclusion is in a good agreement with that reported by Parjapati and Pandaya,[36] that the -N=N– linkage is more coplanar than the –COO– which allows more packing of the linear molecule and thus enhances the thermal stability of compound I compared with compound IV.

Irrespective of the alkoxy chain length, the difference is marked in the case of the electron-withdrawing substituted nitro, and cyano analogues, and becomes smaller as the alkoxy chain lengthened. These results can be explained in terms of two competitive effects: polarisability anisotropy and repulsive forces. The polarisability anisotropy ($\Delta \alpha$) of the whole molecular structure (excluding the substituent X), calculated for compounds of group I as well as those reported previously for compounds III and IV, revealed that $\Delta \alpha$ for compounds I and III increases as the alkoxy chain is lengthened,[25] whereas for compounds IV the reverse is true.[37] In the case of phenyl benzoate molecules (compounds III), the increase in $\Delta \alpha$ with chain length reflects the increase in the lateral aliphatic–aliphatic interactions of the rod-shaped molecules, which adds to the dipole–dipole interactions, as a result of increasing the n-alkane character. Conversely, in the other cases (IV), the decrease in $\Delta \alpha$ reflects the decrease in molecular rigidity and polarity in their structures.

4. Conclusions

4-(4'-Alkoxy phenylazo)phenyl 4''-substituted benzoates (In$_{n,f}$) were prepared and their thermal behaviour characterised. Two types of substituent were used, namely, an alkoxy group of varying length and a small compact polar group, X. All the compounds investigated were found to possess high transition temperatures indicating strong intermolecular association in either the solid or the mesophase. Conjugation between the alkoxy and phenylazo groups, on one side of the molecule, increases the polarity of the azo nitrogen and so stabilises the mesophase. On the other side of the molecule, varying the electronic nature of the substituent X resulted in extremes in the electronic interactions between the substituent and the mesogenic part via the ester carbonyl group. Such differences have led to a significant variation in the mesophase behaviour of the compounds.

On the other hand, extension of the terminal alkoxy chain gives rise to a decrease in the mesophase-isotropic transition temperatures, suggesting that its effect becomes dominant over polarity variation. It was also found that $T_C^{1/2}$ is linearly related to the polarisability anisotropy, of the C$_{ar}$-X bond for all the series investigated.

Comparison of the mesophase thermal stability of In$_{n,f}$ with IIa$_{n,f}$ revealed that in most cases the compound in series II is more stable than its isomer in series I.

Furthermore, comparing the phase stability of the compounds reported here, series I, with the correspondingly substituted phenyl benzoates (III) and 1,4-phenylene bis-(4-substituted)-benzoates (IV) revealed that introducing a phenylazo or PhCOO group into the phenyl benzoate molecule enhances the stability of the solid and mesophases. On the other hand, replacement of the PhCOO group (in IV) by a phenylazo group enhances the stability of the mesophase and lowers the melting temperatures (i.e. increasing $\Delta T$), a property that can be further improved by investigating the mesophase behaviour in their binary mixtures; this will be investigated in future.

Supplemental data

Supplemental data for this article can be accessed here.

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