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Effect of steric factors on mesomorphic stability I. 4-(4-Substituted phenylazo)-1-naphthyl 4-alkoxybenzoates

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Effect of steric factors on mesomorphic stability
I. 4-(4-Substituted phenylazo)-1-naphthyl 4-alkoxybenzoates

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Four homologous series belonging to the family of 4-(4-substituted phenylazo)-1-naphthyl 4-alkoxybenzoates ($\mathbf{I}_{a\text{–}d}$) ($C_nH_{2n+1}O$–C_6H_4–COO–$C_{10}H_6$–N=N–C_6H_4–X) were prepared in which the 4- substituent (X) was varied between CH_3O, CH_3, Cl and NO_2; while, within each homologous series, the number of carbon atoms, n, was varied between 8 and 14. The compounds were characterized by infrared spectroscopy, ^{1}H NMR spectroscopy and elemental analysis. Their mesophase behaviour was investigated by differential scanning calorimetry and polarizing-optical microscopy. The results are discussed in terms of mesomeric, polarizability, and steric effects. In each group of compounds bearing the same alkoxy group, attempts were made to correlate the mesophase–isotropic transition temperatures (T_c) with the polarizability anisotropy, $\Delta\alpha_X$, of bonds to the small compact substituent X.

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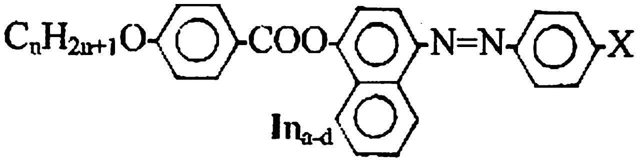
1. Introduction

In studying the problem of relating mesomorphic properties to chemical constitution, the influence of terminal substituents as well as of the core structure has been thoroughly investigated in this laboratory [1–4]. As far as the substituents occupying positions along the sides of the long molecules are concerned, it has been made clear that lateral substitution decreases the thermal stability of both solids and mesophases (smectic and nematic) [5–9]. For example, in a rod-like molecule the 3-chloro substituent (or any substituent larger than a hydrogen atom) increases the breadth of the unsubstituted molecule. Consequently, the long narrow molecules will be forced apart, so reducing the strength of intermolecular lateral attractions. The stability of solids and mesophases depends to a greater or lesser extent on these cohesive forces to maintain the parallel orientations of the molecules. Therefore, lateral substitution will decrease melting (T_m) and clearing (T_c) temperatures. Moreover a side substituent which bridges the 2- and 3-positions, as for example in the case of 4-*n*-alkoxy-1-naphthoic acid [10, 11], has a bulk so great that the compounds are not in fact mesomorphic.

For reasons of technical application, one aims to obtain room temperature liquid crystalline compounds with high mesomorphic thermal stability. It is well known that three-ring molecules posses high mesomorphic stability compared with two-ring molecules. Previously, we have investigated the effect of terminal, polar and long chain substituents on the phase behaviour of two three-ring molecules, namely, the unsymetrically substituted benzoates of hydroquinone [2], and the substituted phenyl azo-alkoxybenzoate [4]. It was found that the addition of the third benzene ring to the phenyl benzoate molecules results in compounds that possess not only high mesophase stability (T_c>200°C), but also high melting temperatures [2, 4]. Furthermore, in both series of compounds nematic and smectic mesophases were observed in varying extents dependent on the polarity of the substituent as well as the length of the alkoxy group.

The goal of the present study is to prepare series of model compounds of low melting point, by replacing the central benzene ring in the azo-ester molecule with a 1,4-naphthalene moiety to give the title compound (**I**). Compounds of structure **I** have been prepared and their mesophase behaviour investigated.



In$_{a\text{-}d}$

I8, n=8; **I**10, n=10; **I**12, n=12; **I**14, n=14 a, X=CH_3O; b, X=CH_3; c, X=Cl; d, X=NO_2

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2. Experimental

Chemicals were purchased from Aldrich, Wisconsin, USA; E. Merk, Darmstadt, Germany; and Fluka, Buchs, Switzerland.

2.1. *Preparation of materials*

2.1.1. ***4-n-Alkoxybenzoic acids (A).*** Firstly, ethyl 4-*n*-alkoxybenzoate was prepared from ethyl 4-*n*-hydroxybenzoate and the appropriate 1-bromo-*n*-alkane; the esters were then saponified to the corresponding acids using alcoholic potassium hydroxide. Details of the method are presented elsewhere [12]. The phase transition temperatures of the resulting acids agreed with the reported literature values [12].

2.1.2. ***4-(4-Substituted phenylazo)-1-naphthol (B).*** One molar equivalent of the 4-substituted aniline in ice-cold dilute hydrochloric acid was diazotized with cold sodium nitrite solution and then added slowly to a cold 1-naphthol/sodium hydroxide solution (1/1). The solid product was filtered and recrystallized twice from glacial acetic acid. The melting points of the prepared azo dyes were in good agreement with literature values [13].

2.1.3. ***4-(4-Substituted phenylazo)-1-naphthyl 4-n–alkoxybenzoates, $In_{a–d}$.*** Molar equivalents of the appropriate naphthol (B) and benzoic acid (A) were dissolved in dry methylene chloride. To the resulting solution, dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)- pyridine (DMAP) were added and the solution stirred for 48 h at room temperature. The separated solid was filtered off and the solution evaporated. The solid residue was recrystallized twice from acetic acid and twice from ethanol to give TLC pure products. The results of elemental analyses agreed with calculated values.

2.2. *Physical characterization*

Calorimetric measurements were carried out using a PL-DSC (Polymer Laboratories, England). The instrument was calibrated for temperature, and heat flow according to the method recommended by Cammenga, *et al.* [14]. The measurements were carried out using 2–3 mg samples sealed into aluminum pans. All the thermograms were recorded at a heating rate of 10°C min^{-1} in a flow of nitrogen (10 ml min^{-1}).

Transition temperatures were obtained, and mesophase type identified using a standard polarizing optical microscope (Wild, Germany), attached to a home-made hot stage.

Infrared spectra (4 000–400 cm^{-1}) were measured with a Perkin Elmer B25 spectrophotometer; ^1H NMR spectra were obtained with a Varian EM 350L.

3. Results and discussion

Since almost identical infrared absorption spectra were observed for all corresponding analogues in the four series (**I**8–**I**14), the absorption bands for compounds of series **I**12, with their assignments, are given as representative examples in table 1. Transition temperatures, as measured by differential scanning calorimetry (DSC), and phases identified by polarizing optical microscopy (POM), for all the compounds investigated are summarized in table 2. Infrared spectra and elemental analyses were consistent with the structures assigned. ^1H-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all the compounds investigated.

3.1. *Infrared absorption spectra*

The almost identical infrared spectra observed for all members of each of the four homologous series, $\mathbf{I}_a$ to $\mathbf{I}_d$, showed that the mesomeric shifts of (i) the ester carbonyl group attached to the 4-position with respect to the alkoxy group and (ii) the azo group attached to the 4-position to the substituent, *X*, are not significantly affected by the length of the alkoxy chain. Furthermore, as can be seen from table 1 for a group of compounds bearing the same alkoxy group, e.g. $\mathbf{I}12_{a–d}$, the ester C=O absorption bands are only slightly influenced by the nature of the polar group *X*. This could be

Table 1. Characteristic infrared absorption frequency (cm^{-1}) for the homologous series $\mathbf{I}12_{a–d}$.

Compound	$–CH_2–$ asym. Stretch.	$–CH_2–$ sym, stretch.	C=O Ester	$–CH_2–$ bending	C–O ester	C–O alkoxy	NO_2	N=N
$\mathbf{I}12_a$	2923.9	2850.6	1730.0	1257.5	1159.1	1074.3	—	1598.9
$\mathbf{I}12_b$	2925.8	2850.6	1724.2	1240.1	1163.0	1080.1	—	1599.0
$\mathbf{I}12_c$	2920.0	2850.6	1730.0	1259.4	1161.1	1078.1	—	1604.7
$\mathbf{I}12_d$	2923.9	2852.5	1732.0	1251.7	1155.3	1074.3	1519.8 asym 1342.4 sym	1600.8

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Table 2. Transition temperatures (°C), enthalpies (kJ mol^{-1}) and entropies (J mol^{-1} K^{-1}) for the homologous series **I**$n_{a–d}$.

Compound	X	T_m ($T_{Cr–N}$)	ΔH_m (kJ mol^{-1})	T_C ($T_{N–I}$)	ΔH_C	ΔS_C
I 8_a	CH_3O	112.7	20.2	178.1	0.71	1.57
I 10_a		108.6	22.6	167.3	0.67	1.52
I 12_a		104.8	13.8	153.0	0.56	1.31
I 14_a		109.6	25.6	142.5	0.33	0.79
I 8_b	CH_3	139.0	21.2	149.8	1.01	2.39
I 10_b		105.7	17.8	148.2	0.63	1.50
I 12_b		115.0	15.0	139.1	0.42	1.02
I 14_b		121.9	11.8	137.3	0.17	0.41
I 8_c	Cl	106.1	21.7	160.5	0.88	2.03
I 10_c		98.8	23.3	138.9	0.71	1.72
I 12_c		105.8	24.9	128.9	0.46	1.14
I 14_c		97.4	24.5	130.1	0.42	1.04
I 8_d	NO_2	152.2	19.4	184.8	0.67	1.46
I 10_d		121.4	23.5	177.6	0.46	1.02
I 12_d		130.4	17.9	168.1	0.29	0.66
I 14_d		131.2	22.6	161.0	0.08	0.18

attributed to their weak inductive effect on the polarization of the ester C=O group through the long phenylazonaphthalene moiety [4]. However, due to variation in the electronic nature of the substituent X, its mesomeric interaction with the remainder of the azo moiety is expected to be somewhat different. In order to investigate the effect of introducing the laterally fused benzene ring, we start with the probable conjugative interaction within the correspondingly substituted phenylazo analogues $C_nH_{2n+1}O–C_6H_4–COO–C_6H_4–N{=}N–C_6H_5–X$, **II**$n_{a–d}$. Thus, in the electron-withdrawing (nitro) substituted homologues (**II**n_d), conjugative interaction takes place between the substituent X and the lone pair of the ester oxygen via the phenylazobenzene moiety, leading to a small increase in the double bond character of the ester C=O group by a positive inductive effect (+I). Consequently, its absorption frequency is increased (figure 1).

Conversely, in the derivatives bearing electron-releasing substituents (CH_3O or CH_3), **II**n_a and **II**n_b, opposite interactions would result in compounds that absorb at lower frequencies. The arylazobenzene group increases, by a negative inductive effect (-I), the single bond character of the C=O bond (figure 2), hence lowering its force constant and, consequently, its absorption frequency [4].

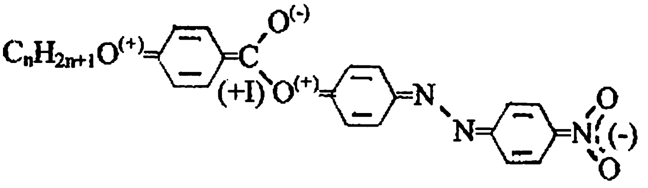


Figure 1. Conjugative interactions within the nitro-substituted derivatives **II**n_d.

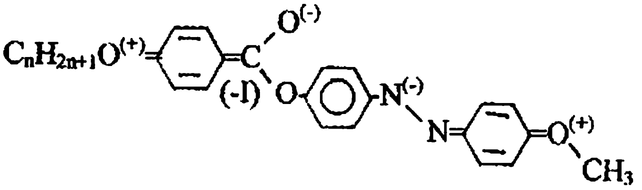


Figure 2. Conjugative interactions within the methoxy-substituted derivatives **II**n_a

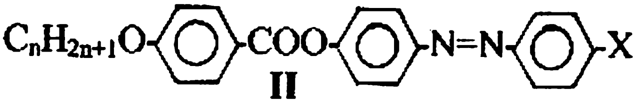
The chloro-substituted derivatives (**II**n_c) occupy intermediate positions between the two extremes **II**n_a and **II**n_d. Turning now to our present series of compounds, i.e. the naphthyl analogues, the bulk of the naphthalene group hinders rotation around the $–O–C_{10}H_6–N–$ bond, thus diminishing the possibility of formation of the conjugated structures represented in figures 1 and 2. As a result, the polar substituents, X, in **I** will hardly transfer its effect on the mesomeric shifts of either the C=O or N=N bonds and, consequently, almost identical values for their absorption bands will be produced (see table 1).

3.2. *Polarizing optical microscopy (POM)*

The mesophases of the investigated compounds were identified using a hot stage polarizing microscope. All compounds exhibit only an enantiotropic nematic phase. By comparison, the phenyl analogues (**II**) exhibit a smectic mesophase transition when nitro or chloro groups are present as terminal polar substituents [4]. The attachment of the laterally fused benzene ring into the three-ring structure (**II**) forces the rod-shaped molecules apart, thus reducing the lateral cohesive forces, a criterion for smectic phase formation.

3.3. *Differential scanning calorimetry*

Transition temperatures for the four homologous series $I_a–I_d$ are collected in table 2, while the variation of these transition temperatures with the alkoxy chain length are depicted in figure 3. All the compounds investigated, irrespective of the substituents X or R, show only the nematic phase and the nematic phase stability (T_C) generally decreases on increasing the alkoxy chain length. The decrease is almost linear in the case of the methoxy- and nitro-substituted derivatives, and tends to



II

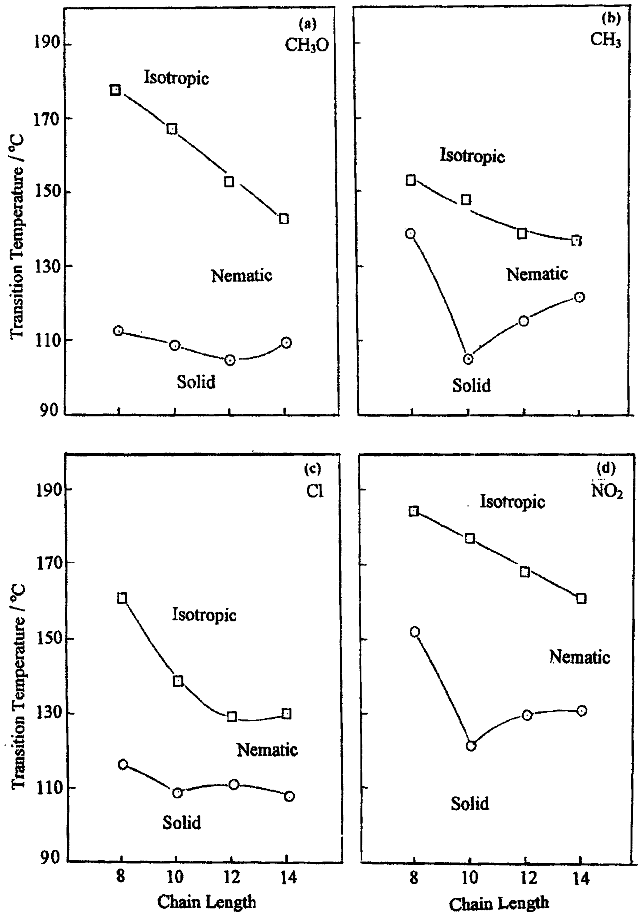


Figure 3. Variation of the nematic – isotropic transition temperature (T_{N-I} or T_c) with the alkoxy chain length (n).

level off for the chloro analogues. This is in good agreement with literature reports [11, 15]. Such behaviour can be attributed to the fact that increasing the alkyl chain length leads to an increase in separation between the aromatic centres, which are highly polarizable and carry the polar substituent X. Therefore, the terminal intermolecular cohesions, responsible for the formation of the nematic phase, will be diminished [11, 15].

Table 3. Clearing temperatures (°C), enthalpies (kJ mol^{-1}) and entropies (J mol^{-1} K^{-1}) for the homologous series **II**n_{a-d}.

Compound	X	T_{SmA-N}	T_C (T_{SmA-I})	T_C (T_{N-I})	ΔH_C	ΔS_C
II8_a	CH_3O	—	—	233.5	1.96	3.81
II10_a		—	—	220.9	1.01	2.04
II12_a		—	—	209.3	1.04	2.16
II14_a		—	—	196.7	1.21	2.58
II8_b	CH_3	—	—	208.9	1.62	3.36
II10_b		—	—	188.1	0.92	2.06
II12_b		—	—	183.9	0.82	1.79
II14_b		—	—	179.9	0.66	1.46
II8_c	Cl	179.3	—	224.2	1.22	2.45
II10_c[a]		—	210.9	—	0.43	0.89
II12_c[a]		—	197.7	—	1.28	2.72
II14_c[a]		—	193.4	—	3.99	8.55
II8_d	NO_2	237.9	—	249.9	0.52	0.99
II10_d[a]		—	230.9	—	0.34	0.68
II12_d[a]		—	221.9	—	1.15	2.32
II14_c[a]		—	215.3	—	6.01	12.30

[a] Derivatives that possess only the smectic A phase.

It is of interest here to recall the literature data, especially those concerning compounds **II**[4] for molecular structures comparable to compounds **I**; corresponding data for compounds **II**n_{a-d} are collected in table 3. The data showed that in compounds of type **II**, the methyl and methoxy analogues, irrespective of the alkoxy chain length, are purely nematogenic. Alternatively, the nitro and chloro analogues exhibit respectively either smectic A and nematic (for n=8), or only smectic A behaviour, upon increasing the alkoxy chain length. Generally, the formation of a smectic, rather than a nematic mesophase is effected mainly by the presence of strong lateral, and weak terminal, cohesion forces between the rod-shaped molecules. The introduction of the laterally fused benzene ring into the mesogenic groups of compounds of type **II** to give compounds **I**n_{a-d} should lead to some steric hindrance and/or enhanced molecular repulsion, due to the increased π- electron cloud on the central naphthalene group. Furthermore, as pointed out from the IR investigation, the naphthalene ring diminishes the mesomeric interaction with the X group, resulting in a less polar compound. This in turn leads to a pronounced depression in the lateral cohesion forces between molecules of compound **I** compared with **II**, and consequently prevents the formation of the smectic A phase, as observed. On the other hand, the terminal cohesive forces responsible for the formation of nematic mesophases [11] are also affected by the replacement of the central benzene ring with the bulky naphthalene moiety, thus decreasing the stability of the nematic phase.

Furthermore, except for compounds **I**8_{a-d}, the nematic mesophase stability of the homologous series I_a–I_d, as observed from figure 3 and table 2, are found to decrease in the order NO_2>MeO>Me>Cl. For series **I**8, the nematic stability order of the chloro- and methyl-substituted derivatives is reversed. The terminal group efficiency, as reported by Gray [11] for a wide range of substituents in a number of mesogenic groups and other systems, is found to decrease in the order MeO>NO_2>Cl>Me. The difference between our order and that of Gray for nematic mesophase stabilities might be attributed to some disordering which takes

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place due to the steric and repulsive effects of the central, laterally fused, benzene ring. The melting points behave differently (figure 3), and show a sudden decrease with increase of n from 8 to 10 followed by gradual increase, in the nitro- and methyl-substituted analogues. For the methoxy derivatives, the decrease in melting points is slight up to $n=12$ then rises again; while for chloro derivatives, there is irregular variation of the melting point with n. This is because thermal stability of the solid state is principally influenced by the attractive forces in the crystalline lattice [16]. Since these short range forces of association are only secondarily related to the molecular structure [16], the melting temperature is not necessarily changed in a regular manner by variation in the molecular structure.

Enthalpies and entropies of transitions (ΔH_C and ΔS_C) of compounds **I** and **II** are included in tables 2 and 3, respectively. It is seen from table 2 that the enthalpies do not correlate well with either the polarity of the substituent or the transition temperature. The most probable explanation may be that in the liquid crystal phases repulsive forces are key in determining mesophase properties. Thus, the relatively low ΔH_C values for the nitro compounds [17, 18] arise from the repulsion between the nitro groups themselves and with the other strongly negative dipoles. On the other hand, the lower ΔH_C and ΔS_C values for compounds **I** compared with **II** are again attributed to the steric effect of the naphthalene group that increases the disorder within the nematic phase.

3.4. *Thermal mesophase stability and polarizability anizotropy of 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 a small compact terminal substituent (C_{ar}–X) was studied by van der Veen [19]. The relation has the form:

$$T_C \propto (\Delta\alpha_M + \Delta\alpha_X)^2 \qquad (1)$$

where T_C is measured in Kelvin. The term $\Delta\alpha_M$ is the anisotropy of the polarizability for all the molecular structure except the terminal substituent X. Equation (1) can be put in the form [20]:

$$T_C^{\frac{1}{2}} \propto (\Delta\alpha_M + \Delta\alpha_X) = a.\Delta\alpha_M + a.\Delta\alpha_X \qquad (2)$$

where a is the proportionality constant. Thus, if $T_C^{\frac{1}{2}}$ is plotted against $\Delta\alpha_X$ for any series of liquid crystalline compounds, a straight line is expected, with slope a and intercept $a.\Delta\alpha_M$. Thus $\Delta\alpha_M$ will be given by: $\Delta\alpha_M$=intercept/slope.

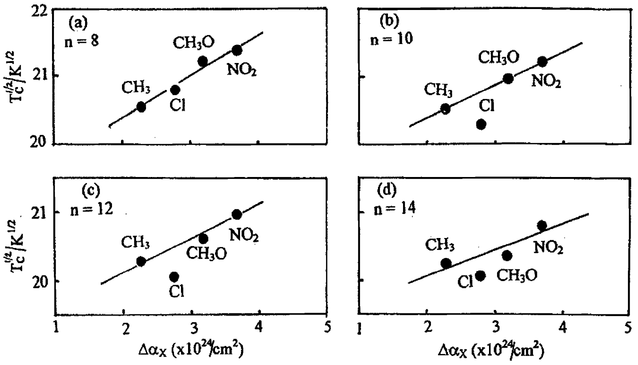

Figure 4. Dependence of $\sqrt{T_c}$ on the anisotropy of polarizability ($\Delta\alpha_x$) for series (*a*) **I**8, (*b*) **I**10, (*c*) **I**12, (*d*) **I**14.

The $T_C^{\frac{1}{2}}$ values are plotted as a function of $\Delta\alpha_X$, for series **I**8–**I**14, as depicted in figure 4. The observed deviations from linear plots can be ascribed to the prohibited conjugation between the substituent X and the mesogenic group due to the presence of the naphthalene group, as already discussed.

4. Conclusions

Four homologous series of the family of compounds, the 4-(4-substituted phenylazo)-1-naphthyl 4-n-alkoxybenzoates, were prepared and their structures elucidated. The phase transitions of the compounds were thermally and optically characterized by DSC and POM, respectively. Two types of substituents were used, namely an alkoxy group of varying chain length and a small compact polar group, X. All the compounds investigated were found to be nematogenic only. Irrespective of the terminal substituent X, the mesophase stability of the compounds was found to decrease systematically with increasing chain length. On the other hand, there was no systematic variation of the melting temperature with alkoxy group length for any of the homologous series. A comparison was made between the **I**$n_{a\text{–}d}$ series and an analogously substituted series, the 4-(4-substituted phenylazo)phenyl 4-n–alkoxy benzoates, **II**$n_{a\text{–}d}$[4]. The results showed that, the lateral introduction of a fused benzene ring into the series **II**$n_{a\text{–}d}$ to give **I**$n_{a\text{–}d}$ results generally in a significant reduction in the mesophase stability (T_C) of the compounds. This reduction is attributed to the steric effect and the repulsive forces between molecules arising from the intense π- electron clouds on the naphthalene centre between neighbouring molecules. A correlation was made between the nematic phase stability T_C and the polarizability anisotropy $\Delta\alpha_X$ of bonds to small compact substituents X. Poor linear correlations, ascribed to the steric effect, were obtained irrespective of the alkoxy chain length.

References

[1] G.R. Saad, R.I. Nessim. *Liq. Cryst.*, **26**, 629 (1999).

[2] M.M. Naoum, T.Y. Labeeb, E. Happ, H. Seliger. *Thermochim. Acta*, **391**, 151 (2002).

[3] M.M. Naoum, R.I. Nessim, G.R. Saad, T.Y. Labeeb. *Liq. Cryst.*, **30**, 165 (2003).

[4] R.I. Nessim, M.M. Naoum, S.Z. Mohamed, M.I. Nessim. *Liq. Cryst.*, **31**, 649 (2004).

[5] R.A. Vora, A.K. Prajapati. *Liq. Cryst.*, **25**, 567 (1999).

[6] A.K. Prajapati. *Liq. Cryst.*, **27**, 1017 (2000).

[7] A.K. Prajapati. *Mol. Cryst. liq. Cryst.*, **348**, 65 (2000).

[8] A.K. Prajapati, H.M. Pandya. *Mol. Cryst. liq. Cryst.*, **393**, 31 (2003).

[9] M. Kaspar, A. Bubanov, V. Hamplova, S. Pikl, Glogarova. *Liq. Cryst.*, **31**, 821 (2004).

[10] G.W. Gray, B. Jones. *J. chem. Soc.*, 683 (1954).

[11] G.W. Gray. *Molecular Structure and the Properties of Liquid Crystals*. Academic Press, London and New York (1962).

[12] G.W. Gray, B. Jones. *J. chem. Soc.*, 4179 (1953).

[13] (*a*) A.C. Sircar. *J. chem. Soc.*, 766 (1916); (*b*) M. Salvatore. *Ann. Chim.*, **59**, 138 (1969).

[14] H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G.W.H. Hoehne, S.M. Sarge. *Thermochim. Acta*, **219**, 333 (1993).

[15] M.J.S. Dewar, J.P. Schroeder. *J. org. Chem.*, **30**, 2296 (1965).

[16] A.W. Levine. *Introduction to Liquid Crystals*. RCA Laboratories, Princeton (1975).

[17] M.J.S. Dewar, A.C. Griffin. *J. chem Soc., Perkin II*, 713 (1976).

[18] R.I. Nessim. *Thermochim. Acta*, **389**, 49 (2002).

[19] J. Van der Veen. *J. Phys., Colloq. C1*, **36**, 375 (1975).

[20] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A. Abdel Aziz. *Liq. Cryst.*, **25**, 73 (1998).

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