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Bashir M. Sheikh-ali^a; Richard G. Weiss^a

^a Department of Chemistry, Georgetown University, Washington, D.C., U.S.A.

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Liquid crystalline behaviour from binary mixtures of non-mesogenic 4-alkyl-*N*-(4-cyanophenyl) piperidines [1]

by BASHIR M. SHEIKH-ALI and RICHARD G. WEISS*

Department of Chemistry, Georgetown University, Washington,
D.C. 20057, U.S.A.

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A relatively rare phenomenon, the induction of thermotropic mesophases from combinations of homologues of non-mesogenic compounds, is examined in some detail. Thus, monotropic nematic phases have been obtained from binary mixtures of 4-alkyl-*N*-(4-cyanophenyl)piperidines (**I**). Except for the hexyl homologue, the compounds **I** with butyl to nonyl as alkyl groups are non-mesomorphic as neat materials. From phase diagrams, the nematic clearing temperatures of the binary mixtures are found to vary linearly with composition and to increase as the molecular lengths of the components are increased. By introducing a methyl group at the 1-position of the alkyl chain, the melting points of the neat components are depressed, and the nematic clearing temperatures of the binary mixtures are lowered. Factors associated with the induction of this mesomorphism and with the 'kinetic' and thermodynamic stabilities of the monotropic nematic phases are discussed. Among these is the orientation *between* the rings of the core groups in **I** and in the more common mesogens, the *trans*-4-alkyl-1-(4-cyanophenyl) cyclohexanes, **II**.

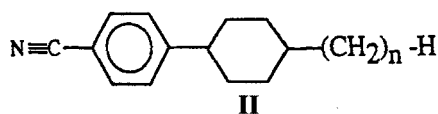
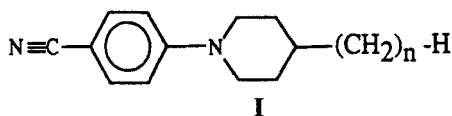
1. Introduction

The formation of liquid crystalline phases from a binary system in which neither component is mesomorphic is very unusual. For instance, Lohar [2] and Bennett and Jones [3] reported that mixtures of 4-methoxy- and 4-ethoxy-benzoic acids exhibit a nematic phase while the individual components are non-mesomorphic; later studies revealed that both compounds have monotropic nematic phases [4]. *p*-Anisal-*p*-phenetidine and *p*-nitrobenzal-*p*-phenetidine were reported to yield nematic mixtures [5], but no mesophases as neat compounds; subsequent studies identified a monotropic nematic phase for *p*-anisal-*p*-phenetidine [6]. However, Lawrence [7] observed mesophase formation in 1:2 binary mixtures of cholesterol and 1-alkanols containing 12, 13, 14, 16 and 18 carbon atoms. Recently, cetyl alcohol and lauric acid mixtures [8] were found to exhibit a lamellar liquid crystalline phase. In the latter two systems, intermolecular hydrogen-bonding must be an important contributing factor to maintaining the necessary aggregation for mesomorphism.

Given the structural similarity between molecules of **I** and *trans*-1-alkyl-4-(4-cyanophenyl) cyclohexanes (**II**), which are known to form enantiotropic nematic and monotropic smectic phases [9], we anticipated that individual homologues of **I** would be mesomorphic. We have investigated the $n = 4$ to $n = 9$ members of the series and find that none, except for the hexyl homologue (which is known to exhibit a monotropic nematic phase below 12°C [10]) is mesomorphic. In a preliminary report [11] we

* Author for correspondence.

noted that binary mixtures of 4-*n*-butyl-*N*-(4-cyanophenyl)piperidine (**I**, $n = 4$) and 4-*n*-heptyl-*N*-(4-cyanophenyl)piperidine (**I**, $n = 7$), designated as 1-47, form monotropic nematic phases. We report here that other binary mixtures of **I** exhibit monotropic nematic phases which, under certain conditions, can be relatively stable [12]. The structural factors influencing the stabilization or destabilization are discussed and composition phase diagrams for other mixtures are reported.



2. Experimental

2.1 Methods

Heats of transitions and the temperatures of maximum heat flow were measured by differential scanning calorimetry (DSC) with a Dupont 1090B thermal analyser and a 910 DSC cell base. Heats of transitions were calibrated using an indium standard [13]; temperatures were calibrated with *n*-butyl stearate [14]. Samples (4–6 mg) of one component systems were weighed directly into an aluminium pan and sealed. For binary mixtures, a sample (c. 20 mg) was heated until all the solid dissolved and then was mixed mechanically; an aliquot was weighed and then sealed in the DSC pan. Samples were reheated in the DSC apparatus to above their clearing temperature, cooled rapidly (c. 10°min^{-1}) to -10°C , and equilibrated there for 15 min before heating. A 2°min^{-1} heating rate and a 1°min^{-1} cooling rate were used throughout. Subsequent cooling thermograms were recorded after the sample had been transformed to the liquid. Optical textures were photographed through crossed polars either with a Nikon FX-35 camera mounted on a Nikon Optiphot microscope using a Mettler FB 82HT hot stage or with a Pentax K1000 camera mounted on a Leitz microscope equipped with a Leitz 585 thermostating stage.

Diethylether (Baker) was distilled from LiAlH_4 or sodium. Isopropyl alcohol (Fisher) was distilled from sodium. Bromoalkanes (97 + per cent, Aldrich) were dried over MgSO_4 . 4-Cyanopyridine (98 per cent, Aldrich), hydrazine (95 per cent, Eastman), 4-fluorobenzonitrile (99 per cent, Aldrich or Alfa), and PtO_2 (Aldrich) were used as received. 4-Acetylpyridine (98 + per cent, Aldrich) was vacuum distilled prior to use. Activated Raney nickel (Aldrich), a 50 per cent slurry in water at pH 10, was neutralized (by washing with water until pH 7 was achieved) before use. Silica gel (Baker Analysed) was 60–200 mesh.

Analytical gas chromatography (GC) was performed using a Perkin–Elmer 4500 gas chromatograph with a flame ionization detector and a HP-17 (50 per cent phenyl and 50 per cent polysiloxane) $50 \text{ m} \times 0.53 \text{ mm}$ wide bore column. IR spectra were recorded on a Perkin–Elmer 457 grating spectrophotometer with polystyrene as reference. ^1H and ^{13}C NMR spectra (CDCl_3/TMS) of dilute solutions were obtained with a Bruker AM-300 WM spectrometer using an Aspect 3000 computer. Mass spectra were obtained with a Fisons Instruments MD 800 GC–MS system which includes a DB-5MS $15 \text{ m} \times 0.25 \text{ mm}$ column.

Both **I** (see [11] for scheme) and analogues containing a methyl group at the 1-position along the alkyl chain (**I-Me**) were synthesized by previously reported methods [15] and purified to > 99 per cent homogeneity according to their GC. IR, mass and ^1H and ^{13}C NMR spectra were in accord with the structures of **I** and **I-Me**. The detailed procedure for the synthesis of one homologue of **I** is given below. Product yields have not been optimized.

Binary mixtures of **I** will be referred to as **I-mn** where *m* and *n* are the number of carbon atoms in the alkyl chain of each component of **I**. When a mixture at specific composition is discussed, the wt/wt ratio of the two components will be cited.

2.2. 4-*n*-Alkyl-N-(4-cyanophenyl)piperidines (**I**)

2.2.1. 4-Heptanoylpyridine (**1a**)

At room temperature, under a nitrogen atmosphere, 10 ml of a solution of 24 g (0.15 mol) of 1-bromohexane in 70 ml of dry ether was added to 3.3 g (0.14 g-atom) of magnesium turnings. After reaction was initiated, the remainder of the bromohexane solution was added dropwise to maintain a gentle reflux. The mixture was heated at reflux for an additional 30 min, cooled, and a solution of 4-cyanopyridine (15 g, 0.14 mol) in dry ether (50 ml) was added. The mixture was boiled for 4 h, cooled in an ice bath, and sequentially 25 ml of ice water and 50 ml of cold 5 M-HCl solution were added. The aqueous phase was separated and the organic layer was shaken with 30 ml of 5 M-HCl. The combined aqueous extracts were heated on a water bath for 1 h, cooled, basified with K_2CO_3 , and shaken with ethyl ether (3×25 ml). The combined organic extracts were dried (Na_2SO_4), filtered, and evaporated to give a residue. Vacuum distillation gave 9.5 g (35 per cent) of 4-heptanoylpyridine, b.p. 112–118°C/1 mmHg. After being passed through a silica gel column (20/80: toluene/hexane as eluant), the product was 95 + per cent pure by GC. IR (neat film): 1680 cm^{-1} ($\nu\text{C}=\text{O}$). ^1H NMR (CDCl_3 , TMS): δ 8.80 (d, $J = 6.0$ Hz, 2 H, aromatic), 7.73 (d, $J = 6.3$ Hz, 2 H, aromatic), 2.97 (t, $J = 7.5$ Hz, 2 H, $-\text{CH}_2-$), 1.74 (p, $J = 7.2$ Hz, 2 H, $-\text{CH}_2-$), 1.4 (m, 6 H, $3-\text{CH}_2-$), 0.90 ppm (t, $J = 6.8$ Hz, 3 H, $-\text{CH}_3$).

2.2.2. 4-*n*-Heptylpyridine (**1b**)

9 g (0.05 mol) of 4-heptanoylpyridine (**1a**) and 15 g (0.5 mol) of hydrazine (95 + per cent) were heated at reflux for 4 h, cooled to room temperature and 30 g of powdered KOH was added. The mixture was boiled until evolution of nitrogen ceased (*c.* 2 h) and cooled. Water (25 ml) was added and the mixture was shaken with ether (3×15 ml). The combined organic extracts were dried (Na_2SO_4), filtered and the solvent was evaporated. Vacuum distillation of the residue gave 7.5 g (90 per cent yield) of 4-*n*-heptylpyridine, b.p. 95–100°C/0.1 mm Hg, which was 98 per cent pure by GC. IR (neat): no peak in the carbonyl region. ^1H NMR (CDCl_3/TMS): δ 8.47 (d, $J = 6.0$ Hz, 2 H, aromatic), 7.09 (d, $J = 5.7$ Hz, 2 H, aromatic), 2.85 (t, $J = 7.5$ Hz, 2 H, $-\text{CH}_2-$), 1.6 (m, 2 H, $-\text{CH}_2-$), 1.3 (m, 8 H, $4-\text{CH}_2-$), 0.88 (t, $J = 6.6$ Hz, 3 H, $-\text{CH}_3$).

2.2.3. 4-*n*-Heptylpiperidine (**1c**)

4-*n*-Heptylpyridine (**1b**, 1.5 g, 0.01 mol) in 18 ml of 1 M-HCl was shaken with 90 mg PtO_2 under 40 psi of H_2 at room temperature in a Parr hydrogenator for 20 h. The mixture was filtered and the filtrate was evaporated under aspirator vacuum. The solid residue was basified with 10 per cent KOH solution (20 ml) and shaken with ether (3×20 ml). The combined organic extracts were dried (Na_2SO_4) and filtered.

After evaporation to give a residue, 1.2 g (77 per cent yield) of 4-*n*-heptylpiperidine (purity > 90 per cent) was obtained. $^1\text{H NMR}$ (CDCl_3/TMS): δ 3.03 (d, $J = 12.0$ Hz, 2 H, $\text{H}_{\alpha,\text{eq}}$), 2.56 (dt, $J = 12.0$, 2.1 Hz, 2 H, $\text{H}_{\alpha,\text{ax}}$), 1.7 (d, $J = 12.9$ Hz, 2 H, $\text{H}_{\beta,\text{eq}}$), 1.6 (broad s, 1 H, N-H), 1.3 (m, 13 H), 1.05 (dq, $J = 12.0$, 3.9 Hz, 2 H, $\text{H}_{\beta,\text{ax}}$), 0.88 (t, $J = 6.6$ Hz, 3 H, terminal $-\text{CH}_3$). $^{13}\text{C NMR}$ (CDCl_3/TMS): δ 47.6, 37.6, 36.6, 34.1, 32.2, 30.1, 29.6, 26.8, 22.9, 14.7 ppm.

2.2.4. 4-*n*-Heptyl-N-(4-cyanophenyl)piperidine (**I**, $n = 7$)

2.5 g (0.014 mol) of 4-*n*-heptylpiperidine (**1c**), 2 g (0.017 mol) of 4-fluorobenzonitrile, 2 g of anhydrous K_2CO_3 , and 25 ml dimethylsulphoxide (DMSO) were stirred at 100°C for 8 h and then cooled. CHCl_3 (25 ml) was added and the mixture was shaken with water. The organic layer was dried (Na_2SO_4), filtered, and evaporated under aspirator vacuum. After being chromatographed (silica gel, 1/4:toluene/hexane as eluent) and recrystallized twice from hexane, the product **I** ($n = 7$) 3.2 g (80 per cent), m.p. $52\text{--}53^\circ\text{C}$, was 99 + per cent pure by GC analysis. IR (neat film): 2220 ($\nu_{\text{C}\equiv\text{N}}$), 1609 (ν_{Ar}), 3000–2850 cm^{-1} ($\nu_{\text{C-H}}$ aromatic and aliphatic). $^1\text{H NMR}$ (CDCl_3/TMS): δ 7.46 (d, $J = 8.7$ Hz, 2 H, aromatic), 6.85 (d, $J = 9.0$ Hz, 2 H, aromatic), 3.83 (d, $J = 12.9$ Hz, 2 H, $\text{H}_{\alpha,\text{eq}}$), 2.84 (dt, $J = 12.5$, 2.2 Hz, 2 H, $\text{H}_{\alpha,\text{ax}}$), 1.78 (d, $J = 12.0$ Hz, 2 H, $\text{H}_{\beta,\text{eq}}$), 1.5 (m, 1 H, H_γ), 1.27 (m, 14 H, aliphatic), 0.88 (t, $J = 13.2$ Hz, 3 H, terminal $-\text{CH}_3$). $^{13}\text{C NMR}$ (CDCl_3 , TMS): δ 153.5, 133.5, 120.3, 114.1, 99.1, 47.9, 36.5, 35.8, 31.9, 31.8, 29.8, 29.3, 26.7, 22.7, 14.1 ppm. Mass spectrum: m/z (rel. intensity), 285 (18), (M^+) 284 (91), 283 (62), 199 (33), 185 (24), 183 (24), 157 (34) 145 (33), 131 (100), 130 (35), 129 (46), 55 (43).

3. Results and discussion

Optical microscopy confirmed that all of the compounds of structure **I** with $n = 4\text{--}9$ (except for the $n = 6$ homologue [10]) and **I-Me** with $n = 5\text{--}8$ are not mesomorphic. Melting points (from heat-flow maxima of DSC heating thermograms) are collected in table 1. The exotherm at 14.5°C for **I** ($n = 6$) {16} in figure 1 (a) and (b) is due to an isotropic–nematic transition; the monotropic phase crystallized within a few minutes (see figure 1 (a)). Although the other homologues of **I** can be supercooled by as much as 30°C , crystallization occurs directly from the isotropic phase.

By contrast, binary mixtures of **I** do form monotropic nematic phases which, upon returning to the solid, separate into crystalline domains highly enriched in one component (as evidenced by changes in the optical micrographs and thermograms of samples heated after being incubated to allow crystallization). This is not a consequence of poor mixing since the isotropic–nematic transition temperatures depend acutely upon the compositions of the samples and the temperatures are reproducible only in well-mixed samples. Typical thermograms from cooling and heating cycles of **I** ($n = 6$) and 1/1 **I-mn** mixtures are shown in figure 1 (c) and (d). The birefringent optical patterns of the materials below their transition temperatures can be distorted easily by tapping on the glass cover slips. Figure 2 shows the Schlieren textures [17] of **I** ($n = 6$) and 1/1 mixtures **I-57** and **I-67** after they had been cooled below their clearing temperatures. Virtually identical patterns were observed for the other nematic mixtures reported. The dark brushes correspond to the extinction positions of a nematic liquid. The points where they meet are singularities or disclinations characterized by the dislocation strength $|s|$ whose value is one-fourth the number of brushes. The existence of point singularities with $|s| = 1/2$ and 1 is indicative of a nematic phase [18]. A number of smectic modifications also show Schlieren textures, but with point singularities

Table 1. Melting points (m.p.) of compounds **I** and **I-Me**.

<i>n</i>	Melting point/°C†	
	I	I-Me
4	41.2	—
5	39.7	22.3
6	29.7	< -50
7	52.5	41.0
8	59.8	59.2
9‡	57.2	—
7'§	70	—

† ± 0.6°C.

‡ Exhibits a solid–solid transition at 34.0°C also.

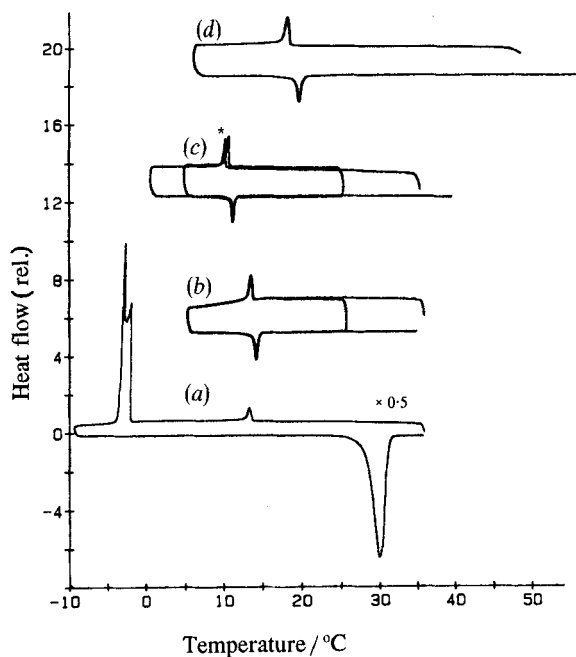
§ 4-(4,6,6-Trimethylheptyl)-*N*-(4-cyanophenyl)piperidine.

Figure 1. DSC cooling–heating thermograms of (a) and (b) both for **I** ($n = 6$), (c) 1/1 **I-56**, and (d) 1/1 **I-57**. Each thermogram represents one of two cooling–heating cycles, starting with cooling (upper curves from the isotropic phase). The asterisk refers to the exotherm of the first cooling run. Except in (a), the samples were not allowed to crystallize on cooling before the heating scan was initiated.

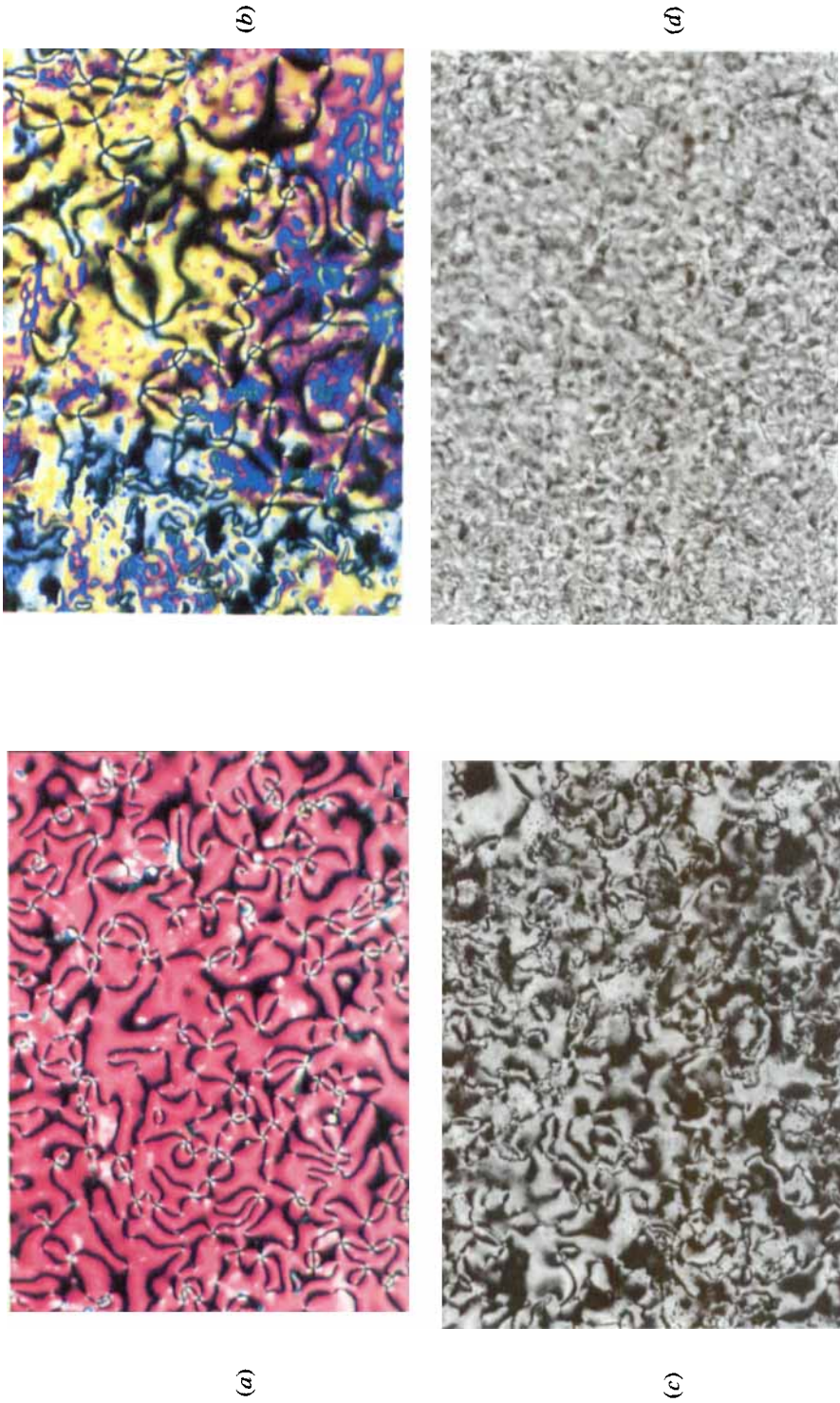


Figure 2. Optical micrographs between crossed polars ($\times 442$) of (a) $1/1 \text{ I } (n = 6)$ at 10°C , (b) $1/1 \text{ I-57}$ at 19°C , (c) $1/1 \text{ I-67}$ at 17°C and (d) $1/1 \text{ I } (n = 5)/\text{I-Me}$ ($n = 8$) at -16°C .

Table 2. Nematic clearing temperatures (T_{N-I}) and transition enthalpies (ΔH) for the binary mixtures of I with a 1/1 composition.

I-mn	$T_{N-I}/^{\circ}\text{C}^{\dagger}$	$\Delta H/\text{Jg}^{-1}\ddagger$
I-45	-6	§
I-46	3.1	2.1
I-47	8.2	2.3
I-48	12	§
I-49	17	§
I-56	11.5	2.6
I-57	18.6	2.7
I-58	22	§
I-79	27	§
I-67	20.0	2.8
$n = 6\parallel$	14.5	2.5

$\dagger \pm 0.5^{\circ}$. $\ddagger 0.3 \text{ Jg}^{-1}$.

§ Transition enthalpies of the very unstable (monotropic) nematic phases could not be measured.

¶ Neat homologue.

characterized by $|s| = 1$ only [17]. The low heats of the mesophase–isotropic transitions of I-mn, $c. 2 \text{ Jg}^{-1}$, are also consistent with nematic–isotropic transitions (see table 2) [19].

The composition phase diagram of I-57 is shown in figure 3. Points on the solid–isotropic curve and on the eutectic line were taken from heat flow maxima of endotherms in DSC heating thermograms of samples which had been cooled from the isotropic phase to -10°C and incubated there for 10 min. The nematic–isotropic curve is from optical microscopic observations on thin samples sandwiched between glass cover slips and heated from the nematic phase. A eutectic composition of 55/45 for I-57 can be estimated from the phase diagram. The eutectic composition, shape of the phase diagram, microscopic textures, and enthalpies of the nematic–isotropic transformations of I-57 are similar to those of I-47 [11]. The ideal behaviour of the nematic clearing temperatures is consistent with the components of the I-mn mixtures being of similar shape. Binary mixtures of cyanobiphenyl homologues, where both components are mesogens, also exhibit ideal clearing behaviour [20].

Since only I ($n = 6$) forms a nematic phase, it may have the most favourable length-to-breadth ratio for mesomorphism. To test crudely this hypothesis, we have attempted to compare the stabilities of the mesophase from I-mn near their eutectic compositions and from I-6 using the magnitudes of the difference between six and $\frac{1}{2}(m+n)$. In this case, ‘kinetic’ stability is indicated by the time required for the isothermal crystallization of the nematic phase to occur; ‘thermodynamic’ stability is reflected in the isotropic–nematic transition temperatures. On these bases, the most ‘stable’ nematic phases of I-mn occur when $|m-n| \leq 13$. Homogeneous nematic phases with lifetimes exceeding several hours could be obtained from mixtures whose components have $\frac{1}{2}(m+n)$ near 6 and when $-10^{\circ} < T - T_{N-I} < 0^{\circ}$. For instance, 1/1 I-56 and I-57 could be kept in their nematic phases for $> 24 \text{ h}$, but 1/1 I-79 was nematic for less than 1 min. Figure 4 provides a similar comparison of clearing temperatures: they increase when the chain of one component is lengthened, while that of the other is kept constant; mixtures containing only shorter homologues have very low clearing temperatures.

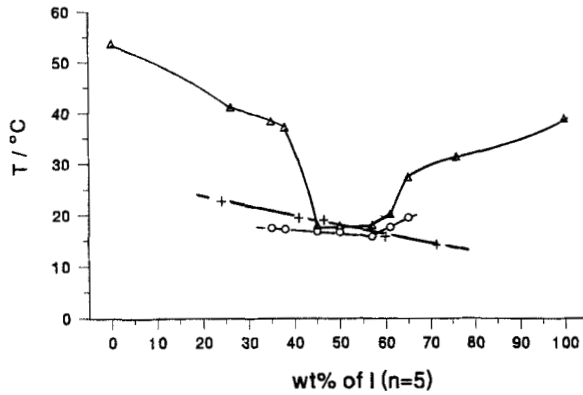


Figure 3. Phase diagram for the system I-57: (○), eutectic melting temperature; (+), nematic clearing temperature; (△), solid-isotropic transition. Lines are intended to show trends between data points.

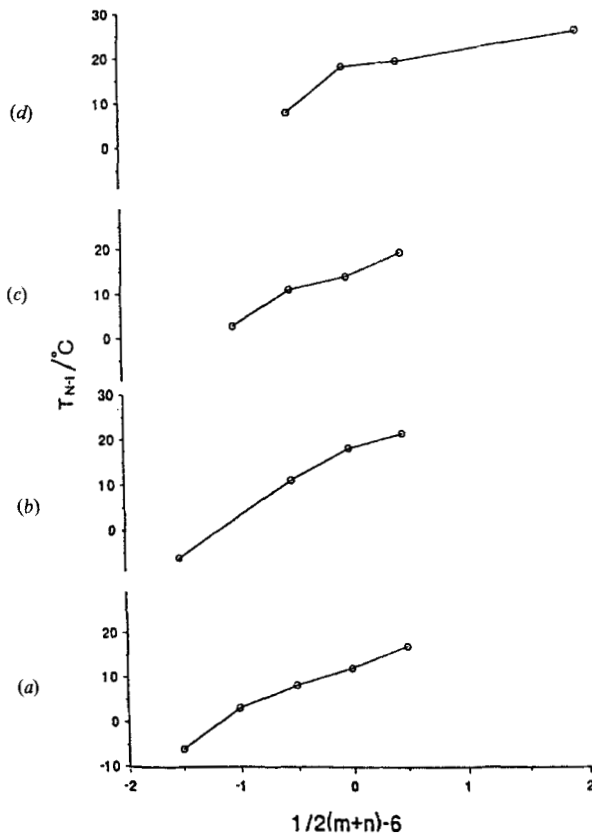


Figure 4. Clearing temperatures, T_{N-I} , versus $\frac{1}{2}(m+n) - 6$ for 1/1 mixtures of I in which one component has (a) $n = 4$, (b) $n = 5$, (c) $n = 6$, and (d) $n = 7$. Lines are intended to show trends between data points.

Table 3. Clearing temperatures (T_{N-I}) and transition enthalpies (ΔH) for 1/1 mixtures of **I** and **I-Me**.

I	I-Me	$T_{N-I}/^{\circ}\text{C}^{\dagger}$	$\Delta H/\text{Jg}^{-1}\ddagger$
4	7	-27.2§	1.1§
5	7	-10.8	1.9
4	8	-20	2.0
5	8	-11	1.6

$\dagger \pm 0.3^{\circ}$. $\ddagger 0.5 \text{ J g}^{-1}$. \S A single run.

The absence of mesophases from all of the neat compounds **I** synthesized, except **I** ($n = 6$), is somewhat puzzling since many of the analogous (*and* isoelectronic) *trans*-1-alkyl-4-(4-cyanophenyl)cyclohexanes (**II**) [9] are known to form enantiotropic nematic and monotropic smectic phases. Although the substitution of a C-H group by nitrogen increases somewhat the conformational liability of the saturated ring, it causes no dramatic structural changes [25]; for instance, the most stable conformation of the piperidyl ring is a chair. However, it does increase the dipole moments of individual molecules: the dipole moments of 4-alkylbenzonitriles are 4.4–4.6 D [21]; that of 4-*N,N*-dimethylaminobenzonitrile is 6.60 D [22].

Crystalline phases of **II** [23], as well as those of other cyanophenyl-containing liquid crystalline materials [24], form head-to-tail complexes in which a cyano group is positioned above the centre of a phenyl ring of a neighbouring molecule. This is not the case at least for the crystalline phases of **I** ($n = 4-8$) [25]. Although the molecules in a unit cell have their directors parallel, as is thought necessary for nematic phase formation [26], the orientation of their cyano groups with respect to each other is not consistent with dipolar interactions being the dominant factor in determining molecular packing. More important, perhaps, is the conformation between the aromatic and cyclohexyl or piperidyl rings. In crystalline **II**, the angle between the aromatic ring and the plane defined by the four methylene carbon atoms of the cyclohexyl ring is ca. 65° [23 (*a*)]. The corresponding angle in the homologues of **I** is only $15-20^{\circ}$ due to overlap between the lone-pair of electrons on the amino-nitrogen atom and the aromatic π -system [25]. *This conformational difference has consequences with respect to the shapes of the cores and to the projections of the alkyl tails from the cores.* An additional consequence of these conformational and electronic differences is that neat phases of **I** appear to have more extensive intermolecular associations than do those of **II** [27].

Thus, **I** ($n = 6$) appears to be anomalous in several respects. Apparently, the molecules of **I** are 'latent' mesogens; as neat compounds they melt at temperatures which provide sufficient energy to destroy the anisotropic interactions necessary to maintain mesomorphic ordering. Packing disorder within the mixtures depresses the melting points below temperatures where nematic phases can exist.

In related studies, methyl-substitution along alkyl chains has resulted in both induction of mesophases in parent molecules which lack them and loss of mesophases in parent molecules which have them [28, 29]. We have attempted to induce mesomorphism in **I** by introducing methyl groups at the 1-carbon of the alkyl chains. Although this substitution serves to depress the melting points [29, 30] of the compounds **I** (referred as **I-Me**) and allows them to be supercooled significantly below their melting temperatures, it does not lead to liquid crystals (see table 1). **I-7'** (see table 1) indicates that more extensive methylation is similarly unsuccessful. As with

I-mn, mixtures of **I-Me** and **I** exhibit nematic phases (see table 3). Figure 2 (*d*) shows the Schlieren texture of a 1/1 **I** ($n = 5$)/**I-Me** ($n = 8$) mixture at -16°C . The domains are smaller and the disclination centres are less pronounced than in nematic **I-mn**, but points with $|\sigma| = \frac{1}{2}$ and 1 can be found. The $1-2\text{J g}^{-1}$ enthalpies of transition to the isotropic phase of mixtures containing **I-Me** are again consistent with our phase assignments [19]. As expected from the depressed melting points of **I-Me**, 1/1 mixtures of **I-Me/I** exhibit clearing temperatures which are *c.* 30° lower than those of 1/1 mixtures of **I** with the corresponding *m* and *n*. Note especially that 1/1 mixtures of **I-Me** ($n = 6$) and another **I-Me** homologue remain isotropic even at -50°C . Thus, branching at the 1-position of the polymethylene chain has a more drastic effect on the nematic clearing points of the mixtures than on the melting points of the neat components.

4. Conclusions

We have found that the packing disorder induced by mixing homologues of 4-*n*-alkyl-*N*-(4-cyanophenyl)piperidines induces the formation of monotropic nematic phases. When the molecular lengths of the components and that of **I** ($n = 6$) differ significantly, the kinetic and thermodynamic stabilities of the induced phases are severely diminished. Methylation of **I** at the 1-position of its alkyl chain causes severe packing disturbances which lead to much lower melting points, but not to nematic phases for the neat compounds. These results, when compared to those found for molecules with isoelectronic phenylcyclohexane rigid cores, suggest the importance of the aromatic-saturated ring conformations as an important factor in permitting or inhibiting mesomorphism.

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