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Liquid crystalline compounds with V-shaped molecular structures: synthesis and characterization of new azo compounds

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Liquid crystalline compounds with V-shaped molecular structures: synthesis and characterization of new azo compounds

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The synthesis and mesomorphic properties of a series of 1,2-phenylene bis[4-(4-alkyloxyphenylazo)benzoates] are reported. The mesophases exhibited by these bent-shaped azo compounds are identified as nematic, smectic A and crystal E phases. All these compounds have fairly low transition temperatures, and so are suitable for physical studies. It has been concluded that the –CH=N– linkage can be more conducive to mesomorphism compared with the –N=N– linkage.

1. Introduction

Although classical thermotropic liquid crystals are commonly composed of rod-like molecules, many other types of low molecular mass compounds with unconventional molecular structures have been shown to exhibit liquid crystalline properties [1]. Jin *et al.* reported bis-[4-(4-butylphenylazo)phenyl] isophthalate as showing no mesophase and concluded that a linear molecular shape is a mesogenic pre-requisite when a compound contains two mesogenic units [2]. However, as long ago as 1929, Vorländer described the liquid crystalline properties of a number of compounds such as bis[4-(4-methoxyphenylazo)phenyl] isophthalate and 1,2-phenylene bis-[4-(4-ethoxyphenylazoxy)benzoate] whose molecules were presumed to have obtuse and acute angled configurations, respectively [3–5]. For the past two decades, such unconventional compounds [6–10] have been attracting attention. However, a spurt of activity in this field was triggered by the recent discovery of banana-shaped liquid crystal materials, i.e. mesogenic compounds with a bend in the middle of the molecules [11, 12]. Very recently, we too have reported [13] the liquid crystalline properties of such banana-shaped mesogens.

A survey of liquid crystals composed of bent-shaped molecules revealed that compounds with azo linkages have hardly been studied [1–6, 12]. This is a surprising fact, as such azo compounds have the following advantages over substances with other linkages like ester, tolane or even the more commonly encountered Schiff's base linkage. Azo compounds are thermally very stable and are attractive from the point of view of studying photo-induced effects. Thus, as a continuation of our work on bent-shaped liquid crystalline compounds, we have focused our interest on such materials. To this end, we designed and synthesized a new homologous series of bent-shaped azo compounds (series 1), whose molecular structures are shown in figure 1. All the homologues of this series are mesomorphic. To test whether the overall temperature range of the mesophases is wider or not in the azo compounds compared with Schiff's bases, we synthesized two further azo compounds A and B whose structures are also shown in figure 1.

2. Experimental

2.1. *General*

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). The ^{1}H NMR spectra were recorded using a 200 MHz Bruker Aveance Series DPX200 NMR spectrometer, with TMS as an internal reference standard. The mass spectra were run on a JEOL JMS 600 Spectrometer. The transition temperatures were determined using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope. The enthalpies of transitions were determined from thermograms obtained by differential scanning calorimetry (DSC7 Perkin-Elmer). The heating and cooling rates were 5°C min^{-1}.

2.2. *Synthesis*

The synthetic route followed to obtain the new compounds of series 1 is shown in the scheme. The experimental details for each step along with the spectral data, are given below.

2.2.1. *Ethyl p-aminobenzoate (2)*

This was prepared following a procedure described previously [14]. To absolute ethanol (80 ml) saturated with dry hydrogen chloride, were added 12 g (0.088 mol)

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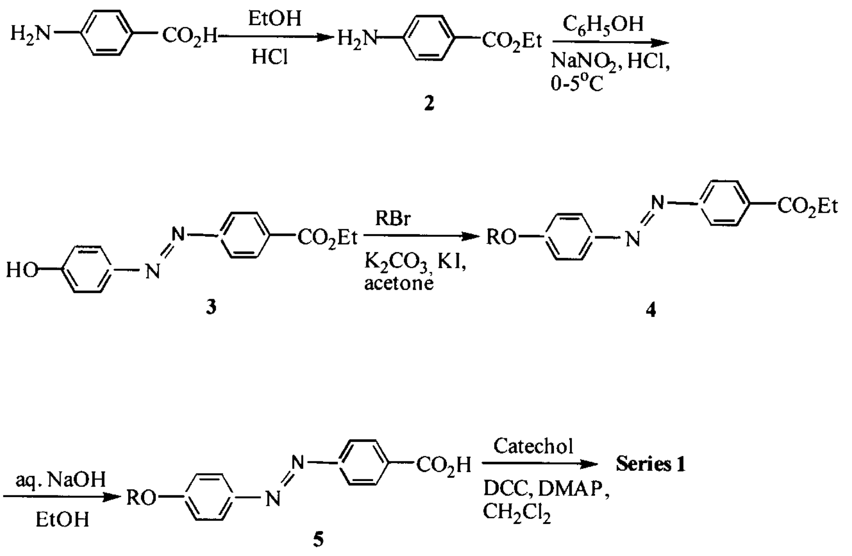

Scheme.

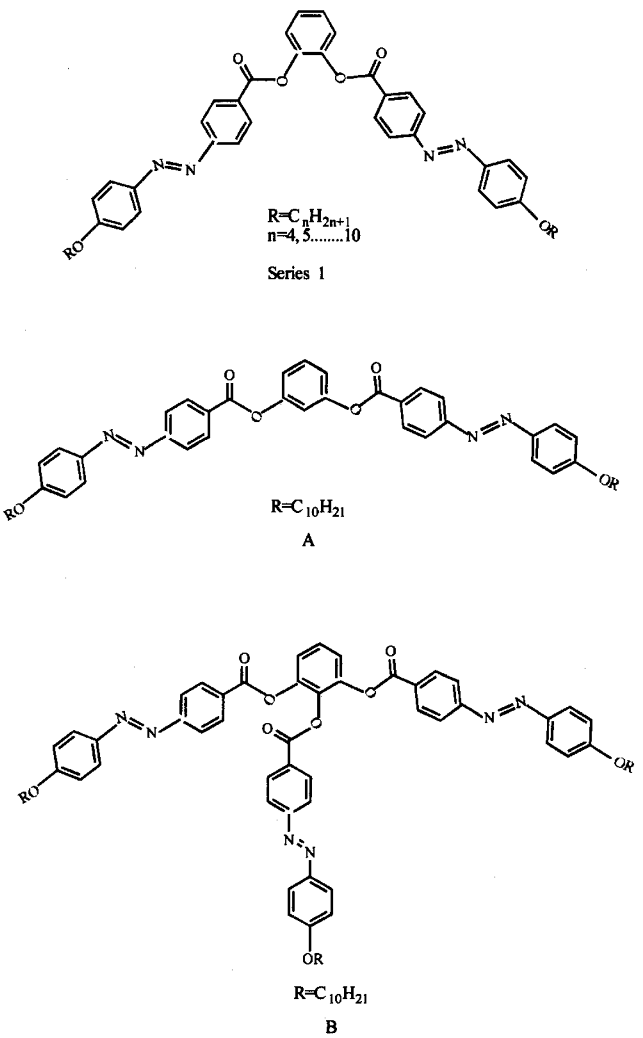

Figure 1. Molecular structures of the different bent-shaped azo compounds synthesized.

of *p*-aminobenzoic acid; the mixture was heated under reflux for 2 h. The hot solution was poured into an excess of water and sodium carbonate added to the clear solution until it was neutral to litmus. The ester **2** was filtered off, dried in air and recrystallized from ethanol; yield, 62%, m.p. 91°C. ^{1}H NMR ($CDCl_3$), δ: 7.8 (d, $J = 8.8$ Hz, 2H, ArH), 6.6 (d, $J = 8.8$ Hz, 2H, ArH), 4.3 (q, 2H, $-CH_2-$), 4.1 (brS, 2H, $-NH_2$), 1.36 (t, $J = 7.0$ Hz, 3H, $-CH_3$).

2.2.2. *Ethyl 4-(4-hydroxyphenylazo)benzoate (3)*

A stirred mixture of compound **2** (8.25 g, 0.05 mol) and 16% HCl (30 ml) was cooled below 5°C and a solution of $NaNO_2$ (3.52 g, 0.051 mol) in water (10 ml) was added dropwise in such a way that the temperature of the reaction mixture was 0–5°C. This cold solution was added dropwise to a cold mixture of phenol (4.9 g, 0.052 mol), NaOH (10 g, 0.25 mol) and water (15 ml). The temperature of this mixture was maintained below 5°C throughout the addition. The product was acidified with dil. HCl, filtered off, dried and recrystallized from aq. ethanol to give the yellow solid **3**; yield 64%. ^{1}H NMR ($CDCl_3$), δ: 8.17 (d, $J = 8.4$ Hz, 2H, ArH), 7.91 (d, $J = 8.8$ Hz, 2H, ArH), 7.88 (d, $J = 8.8$ Hz, 2H, ArH), 6.9 (d, $J = 8.4$ Hz, 2H, ArH), 6.07 (br S, 1H, $-OH$), 4.4 (q, 2H, $-CH_2-$), 1.4 (t, $J = 7.0$ Hz, 3H, $-CH_3$).

2.2.3. *Ethyl 4-(4-decyloxyphenylazo)benzoate (4)*

Compound **3** (2.70 g, 0.01 mol), *n*-decyl bromide (2.65 g, 0.012 mol), K_2CO_3 (2.76 g, 0.02 mol) and a catalytic amount of KI were mixed in 50 ml of acetone. The mixture was heated at reflux for 18 h under nitrogen, cooled to room temperature and poured into cold water (100 ml). The product was extracted into CH_2Cl_2 (50 ml × 3) and the extract wahed with distilled water (100 ml × 3) and dried over Na_2SO_4. The crude product obtained after removal of the solvent was recrystallized twice using ethanol; yield 72%, Cr 98.5°C SmA 102.5°C I. ^{1}H NMR ($CDCl_3$), δ: 8.17 (d, $J = 8.6$ Hz, 2H, ArH), 7.93 (d, $J = 8.6$ Hz, 2H, ArH), 7.89 (d, $J = 8.6$ Hz, 2H, ArH), 7.0 (d, $J = 8.6$ Hz, 2H, ArH), 4.4 (q, 2H, $-CO_2CH_2-$), 4.07 (t, $J = 6.6$ Hz, 2H, $-OCH_2-$), 1.26–1.89 (m, 19H, $-CH_2-$ and $-CO_2CH_2\underline{CH_3}$), 0.88 (m, 3H, $-CH_3$).

2.2.4. *4-(4-Decyloxyphenylazo)benzoic acid (**5**)*

Compound **4** (1.0 g) was dissolved in 95% ethanol (50 ml) and 10% aq. NaOH (2 ml) was added. The mixture was heated at reflux for 6 h, cooled to room temperature, poured into ice cold water (100 ml), and acidified with dil. HCl. The crude product obtained by filtration was recrystallized using EtOH/$CHCl_3$; yield 80%, m.p. 145.0°C. ^{1}H NMR ($CDCl_3$), δ: 8.21 (d, $J = 8.6$ Hz, 2H, ArH), 7.94 (d, $J = 8.8$ Hz, 2H, ArH), 7.92 (d, $J = 8.8$ Hz, 2H, ArH), 7.0 (d, $J = 8.6$ Hz, 2H, ArH), 4.05 (t, $J = 6.6$ Hz, 2H, $-OCH_2-$), 1.27–1.9 (m, 16H, $-CH_2-$), 0.88 (m, 3H, $-CH_3$).

2.2.5. *1,2-Phenylene bis[4-(4-decyloxyphenylazo)-benzoate] (series 1)*

Compound **5** (0.382 g, 0.001 mol), catechol (0.055 g, 0.0005 mol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were dissolved in dry CH_2Cl_2 (50 mol). To this was added 1,3-dicyclohexylcarbodiimide (DCC) (0.247 g, 0.0012 mol) and the reaction mixture was stirred at room temperature for 24 h under nitrogen. The dicyclohexylurea formed was removed by filtration. The crude product obtained on evaporation of the filtrate was recrystallized several times using EtOH/$CHCl_3$; yield 52%. ^{1}H NMR ($CDCl_3$), δ: 8.20 (d, $J = 8.8$ Hz, 4H, ArH), 7.89 (d, $J = 9.0$ Hz, 4H, ArH), 7.83 (d, $J = 8.8$ Hz, 4H, ArH), 7.41 (m, 4H, ArH), 6.97 (d, $J = 9.0$ Hz, 4H, ArH), 4.03 (t, $J = 6.4$ Hz, 4H, $-OCH_2-$), 1.27–1.84 (m, 32H, $-CH_2-$), 0.88 (m, 6H, $-CH_3$); *m/z* (FAB): 838 $[M]^+$ (calculated for $C_{52}H_{62}O_6N_4$).

All the other homologues of series 1 were prepared by a similar method and the spectral data obtained for these compounds were satisfactory.

2.2.6. *Compound A*

This was prepared by following the procedure described for the compounds of series 1. Here, 1.3-dihydroxybenzene was used instead of catechol; yield 48%, m.p. 147.5°C. ^{1}H NMR ($CDCl_3$), δ: 8.33 (d, $J = 8.6$ Hz, 4H, ArH), 7.97 (d, $J = 8.6$ Hz, 4H, ArH), 7.95 (d, $J = 9.0$ Hz, 4H, ArH), 7.52 (m, 1H, ArH), 7.24 (m, 3H, ArH), 7.03 (d, $J = 9.0$ Hz, 4H, ArH), 4.06 (t, $J = 6.6$ Hz, 4H, $-OCH_2-$), 1.28–1.83 (m, 32H, $-CH_2-$), 0.88 (m, 6H, $-CH_3$); *m/z* (FAB): 838 $[M]^+$ (calculated for $C_{52}H_{62}O_6N_4$).

2.2.7. *Compound B*

The synthetic procedure was similar to that for series 1. Here, 1,2,3-trihydroxybenzene was used instead of catechol; yield 47%, m.p. 132.5°C. ^{1}H NMR ($CDCl_3$), δ: 8.18 (m, 6H, ArH), 7.81 (m, 12H, ArH), 7.43 (m, 3H, ArH), 6.96 (m, 6H, ArH), 4.0 (m, 6H, $-OCH_2-$), 1.27–1.80 (m, 48H, $-CH_2-$), 0.88 (m, 9H, $-CH_3$); *m/z* (FAB): 1219 $[M + 1]^+$ (calculated for $C_{75}H_{90}O_9N_6$).

Table. Transition temperatures (°C) and $\Delta S/R$ values of transitions in *italics* for the compounds of series 1. Values in parentheses indicate monotropic mesophase.

n	Cr		E		SmA		N		I
4	•	150.2	•	(93.0)[a]	•	(128.0)	•	163.0	•
		12.69				*1.03*		*0.04*	
5	•	144.6	•	(90.0)[a]	•	(143.4)	•	155.6	•
		13.19				*1.46*		*0.03*	
6	•	132.8	•	(117.8)	•	145.0	•	154.5	•
		12.79		*3.57*		*1.33*		*0.02*	
7[b]	•	120.3	•	(80.6)	•	152.0	•	155.6	•
		5.11		*2.25*		*0.85*		*0.05*	
8	•	101.4	•	(76.4)	•	155.0	•	157.5	•
		11.73		*4.11*		*1.53*		*0.10*	
9	•	94.3	•	(75.5)	•	157.8	—		•
		10.23		*3.03*		*1.79*			
10	•	98.8	•	(97.1)	•	159.4	—		•
		18.79		*3.24*		*2.34*			

[a] Enthalpies could not be measured due to the onset of crystallization.

[b] There is a Cr–Cr transition at 106.6°C (*7.37*).

3. Results and discussion

Before discussing the mesomorphic properties of the homologous 1,2-phenylene bis[4-(4-alkyloxyphenylazo)-benzoates], we briefly mention the observations on the two intermediate compounds **4** and **5** which were found to be liquid crystalline [15]. All the esters **4** exhibit only a SmA phase which is monotropic for the compound with $n = 4$, but enantiotropic for the other homologues. All the compounds exhibited a focal-conic fan-shaped texture on polarizing optical microscopy. In contrast, the acids **5** were found to be polymesomorphic. While an enantiotropic nematic mesophase is common to all the homologues, the compounds with $n \geqslant 7$ exhibit an enantiotropic SmC phase as well. Further, all these acids show some higher order mesophases, the characterization of which needs structural studies to be performed.

The table gives the transition temperatures and $\Delta S/R$ values for the compounds of series 1. Except for the two higher homologues, i.e. the compounds with $n = 9$ and 10, they all exhibited an enantiotropic nematic phase, in addition to the smectic A and crystal E phases. The compounds with $n = 9$ and 10, showed only two phases, viz. smectic A and crystal E. The crystal E mesophase remained monotropic throughout the series. Photomicrographs of the mesophases, i.e. the smectic A and crystal E phases exhibited by the compound with $n = 8$, are shown in figure 2. The DSC thermogram for the same compound is shown in figure 3. As can be seen from the DSC thermogram, we get three peaks on first heating corresponding to the Cr–SmA, SmA–N and N–I transitions. On cooling, again there are three peaks, the first two corresponding to the I–N and N–SmA transitions. However, by reference to the microscopic observations, we can say that the lowest temperature peak now corresponds to the SmA–E transition. No crystallization peak was seen down to − 50°C; but when the sample was reheated, we found an exothermic peak around 62°C. However, on further heating, the first endothermic peak appeared at 101.4°C, which corresponds to the Cr–SmA transition. Therefore, we believe that the exothermic peak around 62°C on reheating is due to 'cold crystallization'. To confirm this, the DSC scans were repeated many times, and the exothermic peak always appeared on reheating and is therefore due to crystallization. To make sure of the existence of the monotropic crystal E phase, we cooled the sample till the SmA–E transition peak occurred and reheated the sample immediately. As expected, we found the E–SmA transition peak at 76.4°C and the next peak at 155.0°C, corresponding to the SmA–N transition. All the compounds with $n \geqslant 6$ behaved in a similar fashion. For the compounds with $n = 4$ and 5, we could see the onset of crystallization both in the microscope and in the DSC thermogram.

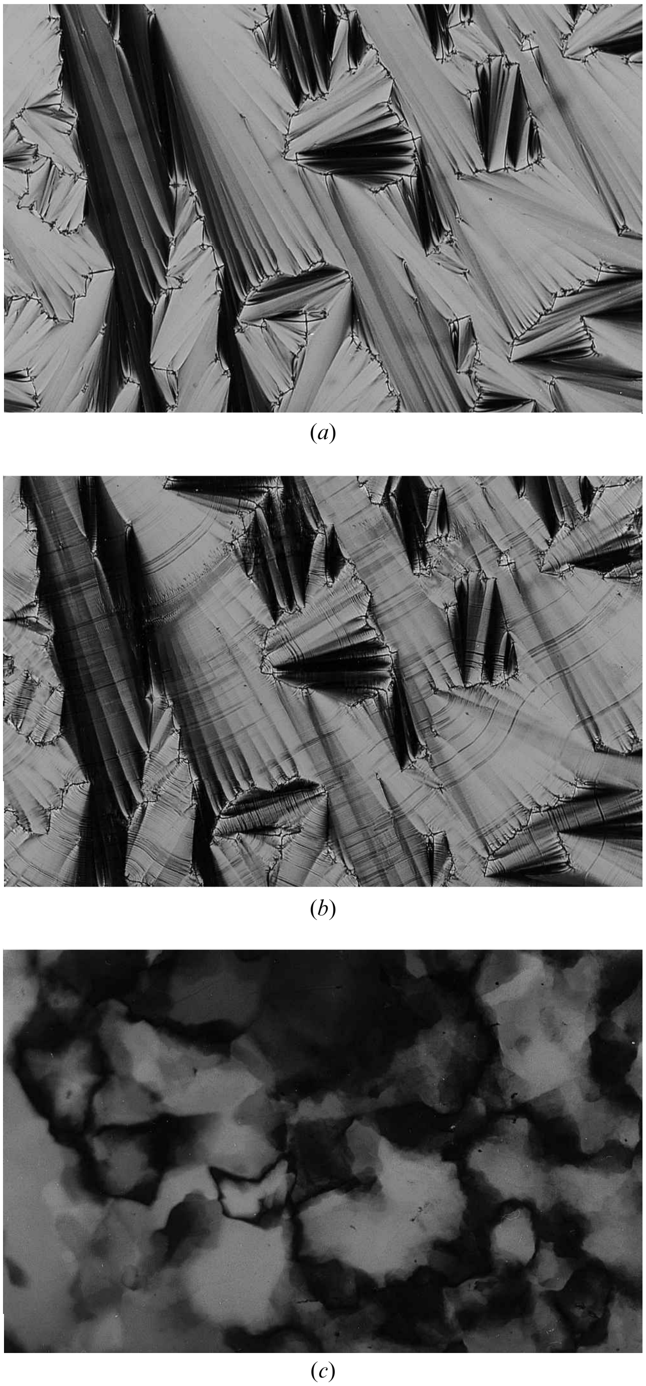

Figure 2. Photomicrographs showing (*a*) the focal-conic fan-shaped texture of smectic A (151.5°C), (*b*) the focal-conic fan-shaped texture with concentric arcs of crystal E (71.0°C), and (*c*) the platelet texture of crystal E phase obtained on cooling the homeotropic texture of the smectic A phase (73.0°C), as exhibited by the compound with $n = 8$.

A plot of transition temperatures vs. the number of carbon atoms in the alkyloxy chains for the compounds of series 1 is shown in figure 4. As can be seen, the

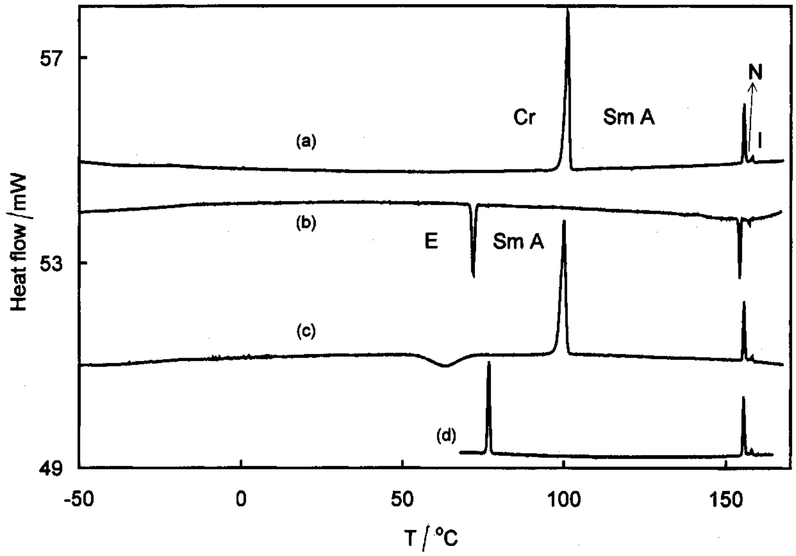

Figure 3. DSC thermograms for the compound with $n=8$. The heating/cooling rate was 5°C min^{-1}. Scan (*a*) represents the first heating, showing three peaks for the Cr–SmA, SmA–N and N–I transitions, respectively. Scan (*b*) represents the first cooling, showing three peaks for the I–N, N–SmA and, the lowest one, SmA–E transitions, respectively; note that no crystallization peaks is observed until -50°C. Scan (*c*) represents the reheating of the sample from -50 to 170°C; note the first exothermic peak corresponding to crystallization of the sample, due to 'cold crystallization', which is absent in the first heating scan (*a*) during the heating process. Scan (*d*) proves the existence of the monotropic crystal E mesophase.

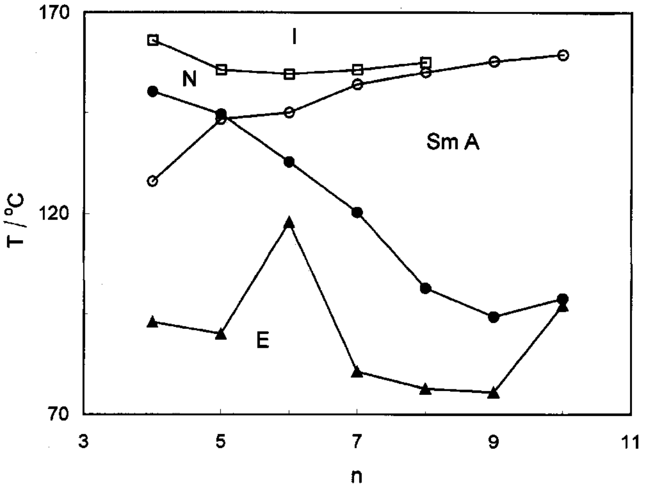

Figure 4. Plot of transition temperatures (°C) vs. the number of carbon atoms (*n*) in the alkyloxy chains for the compounds of series 1.

nematic mesophase range is a maximum for the compound with $n=4$ (12.8°C) and then narrows as far as the compound with $n=8$ (2.5°C). The SmA–N/I curve, shows a gradual increase with the increase in *n*. The smectic A mesophase range is found to be a maximum (63.5°C) for the compound with $n=9$; it then decreases to 60.5°C for the compound with $n=10$. All these observations are in agreement with the general trends for compounds of a homologous series.

We compared the transition temperatures and the nature of the mesophases exhibited by the compounds of series 1 with those reported for 1,2-phenylene bis-[4-(4-alkyloxyphenyliminomethyl)benzoates] [10], to see the relative effects of –CH=N– and –N=N– linkages on the mesomorphism. We found that they behave in quite a similar fashion. Both the series exhibit enantiotropic nematic and smectic A mesophases. In addition, the imino compounds showed a monotropic crystal B phase whereas the azo compounds exhibited a monotropic crystal E phase. Although the transition temperatures of the azo compounds are comparatively lower, the mesophase range is found to be wider for the imino compounds. The values of transition enthalpies for the different transitions are comparable in both series.

Then we synthesized compounds A and B (figure 1), anticipating them to be liquid crystalline, but they were found to be non-mesomorphic. When the –N=N– linkage is replaced by the –CH=N– linkage in both compounds A [11] and B [10], they are however found to be liquid crystalline. This shows that, in this structural context, the –CH=N– linkage is more conducive to mesomorphism than the –N=N– linkage.

4. Conclusions

With the aim of studying the mesomorphic properties of bent-shaped azo molecules, we have synthesized a series of compounds wherein all the homologues exhibit mesomorphic properties, giving classical nematic and smectic mesophases. The −CH=N− linkage is found to be more conducive than the −N=N− linkage to mesomorphism in certain cases, but the advantage of liquid crystalline azo compounds over their imino counterparts is that the former are thermally more stable than the latter. The presence of the azo linkage in liquid crystalline compounds also makes them suitable for physical studies of for example photoinduced effects.

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