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Liquid Crystalline Properties of 4-Methyl-, 4-Ethyl- and 4-Propyl-4′-alkyloxyazobenzenes*

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Liquid crystalline properties of 4-methyl-4′-alkoxyazobenzenes (azo-1-n), 4-ethyl-4′-alkoxyazobenzenes (azo-2-n) and 4-propyl-4′-alkoxyazobenzenes (azo-3-n) are described. For these three homologous series, temperatures and enthalpies of phase transitions and the types of mesophases are presented. The influence of the alkoxy chain length on the sequence of mesophases, temperatures of the phase transitions and the entropy effects are discussed.

Key words: liquid crystals, nematic, smectic, azo compounds, entropy, DSC calorimetry

Azobenzenes are very old liquid crystalline compounds [1], not fully recognized till now from the point of view of their photochemical instability and useless as materials for display devices. However, now these materials are especially interesting in nonlinear optics as photo-chromic materials and photo-switches [2,3].

The main interest in azobenzenes is connected with the simplicity of synthesis, convenient temperature range of mesophases and a rich polymorphism. The simplest structures of azobenzenes are the 4, 4′ alkyl or alkoxy derivatives. The most difficult in synthesis are 4-alkyl-4′-alkyl derivatives and, therefore, only 3 families (4-methyl-4′-alkylazobenzenes, 4-ethyl-4′-alkylazobenzenes and 4-propyl-4′-alkylazobenzenes) were described [4,5,6]. These compounds reveal only nematic and rarely smectic A mesophases, mostly monotropic. From the 4-alkoxy-4′-alkoxyazobenzenes all 12 families were described [7,8,9], where nematic, smectic C and smectic I mesophases were recognized. Interesting is the problem of polymorphism in the unsymmetrical molecules of 4-alkyl-4′-alkoxyazobenzenes. Among derivatives with short alkyl and alkoxy chains Pohl *et al*. found only nematic mesophases [10]. In the 4-nonyl-4′-alkoxyazobenzenes family for the longest alkoxy chain, from octyl derivative, Demus *et al*. [11] found a very rich polymorphism with five mesophases: nematic, SmA, SmC, SmI and SmG. Similar topology we have found in 4-butyl-, 4-pentyl-, 4-hexyl- and 4-heptyl-4′-alkoxyazobenzenes [12,13].

This paper presents the liquid crystalline properties of the first three families: 4-methyl-, 4-ethyl- and 4-propyl-4′-alkoxyazobenzenes, with the shortest alkyl chains. From the 45 synthesized compounds 25 are described for the first time accord-

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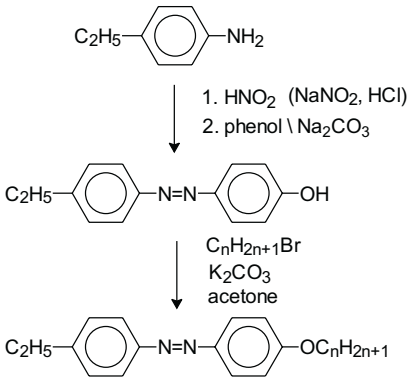
*Dedicated to the memory of Professor Krzysztof Pigoń.

ing to data base [14]. The influence of both, very short alkyl and alkoxy, chains on the phase topology and the entropic effects of the liquid crystalline phase transition are discussed.

EXPERIMENTAL

Synthesis. The main root of synthesis is presented in Scheme 1.

4-Toluidine and 4-ethyl-aniline were used as commercially available Merck products and 4-propylaniline was synthesized according to the procedure described by Keller [15].



Scheme 1. Main root of synthesis 4-ethyl-4′-alkyloxyazobenzenes.

4-Ethyl-4′-hydroxyazobenzene was synthesized by the method of Hillemann *et al*. [16]. A strongly stirred mixture of 4-ethylaniline (68 g, 0.5 mol) and 16% HCl (300 ml) was cooled below 5°C and the solution of $NaNO_2$ (35.2 g, 0.51 mol) in water (100 ml) was added dropwise in such a way that the temperature of mixture was in the range 0°C–5°C. This cold, dark solution was added dropwise to the cold mixture of phenol (47 g, 0.5 mol), Na_2CO_3 (100 g, 2.5 mol) and water (150 ml). The temperature of this mixture was kept all the time below 5°C. The mixture was acidified by HCl. The crude precipitate was filtered, dried and several times recrystallized from hexane to obtain yellow crystals (100 g, 0.4 mol, 79% yield). M.p. 86°C, ^{1}H NMR ($CDCl_3$), δ: 0.95 (3H, t, CH_3), 2.65 (2H, m, CH_2-Ph), 6.00 (1H, s, Ph-OH), 6.90 (2H, d, Ph-H), 7.28 (2H, d, Ph-H), 7.81 (2H, d, Ph-H), 7.87 (2H, d, Ph-H).

4-Ethyl-4′-nonyloxyazobenzene. A mixture of 4-ethyl-4′-hydroxyazobenzene (4 g), 1-bromononane (10 g) and anhydrous K_2CO_3 (30 g) in acetone (50 ml) was refluxed for 48 h. Next, the reaction mixture was filtered and acetone was distilled off from filtrate to give crude yellow precipitate, which was several times recrystallized from methanol and acetone. The final product was two times purified by flash column chromatography (Fluka silica gel 60 mesh, $CHCl_3$ as an eluent), recrystallized from acetone and a few times melted in vacuum (90% yield); ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t, CH_3), 1.06 (3H, t, CH_3), 1.29 (10H, m, CH_2), 1.83 (4H, m, CH_2), 2,72 (2H, q, CH_2-Ph), 4.00 (2H, t, Ph-OCH_2), 6.97 (2H, d, Ph-H), 7.30 (2H, d, Ph-H), 7.80 (2H, d, Ph-H), 7.87 (2H, d, Ph-H).

Equipment. The purity of final compounds and intermediates was monitored by thin layer chromatography (TLC), confirmed by ^{1}H NMR spectroscopy (Bruker AMX 300 MHz) and HP 5890II gas chromatography with a mass selective detector HP5974A. Microanalyses were performed by using Perkin Elmer 2400 CHN Elemental Analyzer. Transition temperatures were measured with a Linkam THMS 600 hot stage and TMS 93 control unit in conjunction with Olympus BX60P polarizing microscope and were confirmed by DSC (Perkin Elmer DSC7, 5 K/min). Thermo-optic set-up was described elsewhere [17].

RESULTS AND DISCUSSION

The first two families reveal only two mesophases, nematic and smectic A, which were identified by polarizing microscopy. All parameters of the phase transitions for azo-1-n and azo-2-n are shown in Tables 1 and 2. Almost all observed mesophases are monotropic (phase transition temperatures are below the melting point). Therefore, our results do not coincide with described previously [14]. Very pure compounds often exhibit a small hysteresis. These disagreements are presented in Tables, whereby the recrystallization temperatures were recorded with the same scan rate 5°C min^{-1}. In the first series (Figure 1) only two derivatives reveal enantiotropic mesophase, pentyloxy (azo-1-5) and dodecyloxy (azo-1-12).

Table 1. Temperatures (°C) and enthalpies (kJ·mol^{-1}) of the 4-methyl-4′-alkoxyazobenzenes. a – phase transition observed only in polarizing microscopy; in square brackets enthalpy of the phase transition; in round brackets temperature of the monotropic phase transition.

m	Melting	Recrystallization	SmA		N		Izo
1	112.0 [61.43]	105.6 [54.47]			•	(64.0) a	•
2	119.2 [73.14]	108.0 [64.35]			•	(90.0) a	•
3	92.0 [62.77]	61.5 [64.35]					•
4	77.1 [58.88]	56.4 [56.61]			•	(74.1) [2.63]	•
5	51.6 [60.18]	44.8 [57.78]			•	62.0 [1.42]	•
6	72.4 [88.81]	63.9 [99.09]			•	(71.3) [2.39]	•
7	76.3 [95.70]	55.8 [90.30]			•	(69.0) [2.16]	•
8	80.4 [127.1]	78.0 [126.6]					•
9	80.1 [120.7]	77.8 [121.9]					•
10	77.7 [123.1]	74.7 [105.3]			•	(76.9) [3.63]	•
11	82.8 [117.9]	81.1 [103.6]					•
12	75.4 [106.9]	72.6 [105.1]			•	76.9 [4.43]	•
14	78.4 [153.3]	63.0 [127.6]	•	(72.0) [5.74]	•	(75.0) [11.59]	•
16	82.5 [145.3]	68.0 [132.2]	•	(71.6) [11.32]	•	(73.0) [18.80]	•
18	81.7 [140.4]	76.9 [146.7]					•

Table 2. Temperatures (°C) and enthalpies (kJ·mol^{-1}) of the 4-ethyl-4′-alkoxyazobenzenes. a – phase transition observed only in polarizing microscopy; in square brackets enthalpy of the phase transition; in round brackets temperature of the monotropic phase transition.

m	Melting	Recrystallization	SmA		N		Izo
1	77.4 [57.74]	48.6 [62.02]			•	(41.0) a	•
2	99.2 [67.33]	74.9 [61.89]			•	(75.0) [1.38]	•
3	87.7 [51.60]	69.4 [65.03]					•
4	66.8 [70.40]	59.2 [69.55]			•	(62.4) [1.03]	•
5	72.7 [68.97]	49.9 [76.96]			•	(54.6) [1.17]	•
6	65.9 [74.26]	51.5 [70.36]			•	66.8 [1.74]	•
7	72.7 [83.47]	61.4 [90.53]			•	(64.2) [1.64]	•
8	69.6 [90.09]	47.5 [81.65]	•	(47.8) a	•	70.0 [2.12]	•
9	72.8 [99.29]	69.0 [95.35]			•	(67.1) [2.79]	•
10	69.7 [103.1]	58.7 [91.49]	•	(60.9) [8.18]	•	71.3 [3.38]	•
11	71.5 [136.1]	65.5 [142.3]			•	(68.1) [3.85]	•
12	68.5 [101.3]	58.2 [91.11]	•	(65.8) [12.27]	•	69.6 [4.33]	•
14	68.0 [75.19]	52.0 [80.66]					•
16	68.0 [97.12]	50.0 [96.25]					•
18	65.0 [88.13]	58.0 [86.75]					•

The second series (azo-2-n) exhibits a richer polymorphism than the first-one (Figure 2). Very interesting is the even-odd effect of the clearing temperature. In the first series high melting and recrystallization temperatures disturb proper topology. The second series exhibits almost all monotropic clearing temperatures, but the even-odd effect is well evident. The best shape of this effect exhibits the third family. Each clearing temperature is enantiotropic, except the propoxy derivative.

The first three members of each series show significantly higher melting temperatures than others and, therefore, the polymorphism is poor. It is connected with the symmetry of molecules and significantly high entropic effects in the melting process. Extraordinary is the behaviour of the octyl, nonyl and undecyl derivatives of the first series, where an unexpected high melting temperature occurs.

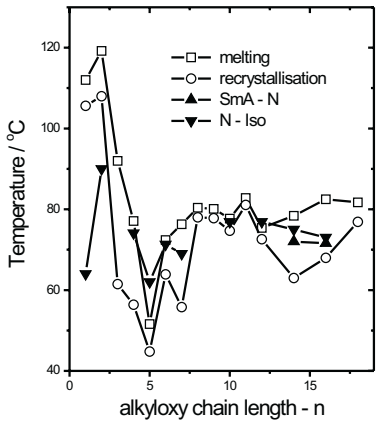


Figure 1. Phase diagram of the 4-methyl-4′-alkoxyazobenzenes.

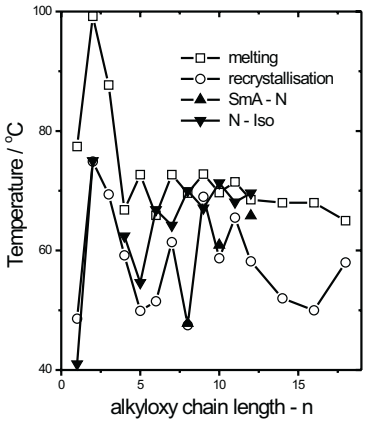


Figure 2. Phase diagram of the 4-ethyl-4′-alkoxyazobenzenes.

In the first series only two members reveal monotropic smectic A phase (azo-1-14 and azo-1-16). The second series reveals three derivatives with the smectic A mesophases (azo-2-8, azo-2-10 and azo-2-12). It is easy to understand, why this polymorphism is so poor. The melting temperatures are too high, covering the possible phase transition temperature. It is important that in the first two families only smectic A mesophase is observed, whereas in the families with 4-alkyloxy-4′-alkyloxyazobenzenes the smectic C mesophase is observed and only few derivatives reveal the smectic A phase [5].

A more complex polymorphism was found in the third series, 4-propyl-4′-alkoxyazobenzenes (azo-3-n). The temperatures and enthalpies of the phase transitions are presented in Table 3 and Figure 3. There exist nematic, smectic A, smectic C and smectic I phases. The nematic phase is present from the methoxy derivative (azo-3-1) to dodecyloxy (azo-3-12), except the propoxy (azo-3-3). The derivatives

from octyloxy (azo-3-8) to hexadecyloxy (azo-3-16) reveal the smectic A phase. Only two members of this series, octyloxy (azo-3-8) and nonyloxy (azo-3-9) reveal smectic C phase, which is monotropic and very narrow. From decyloxy derivative (azo-3-10) to hexadecyloxy (azo-3-16) the tilted, more oriented smectic I phase is present. The phase transition temperatures N-Iso for the longer alkoxy chains are similar, nearly 80°C. Temperatures of the phase transition SmA-N exhibit a different dependence. The increase of this temperature with the alkyloxy chain length is very fast, 52.3°C for octyloxy derivative (azo-3-8) and 77.1°C for dodecyloxy (azo-3-12). The next two members (azo-3-14 and azo-3-16) exhibit phase transition SmA-Iso at nearly 80°C. There exists no nematic phase. Similar properties are observed for other series (azo-4-n, azo-5-n, azo-6-n and azo-7-n) [12,13]. In series azo-3-n the largest amount of mesophases equals three (trimorphism). Entropic effects of the phase transitions N-Iso are not typical (Figure 4). The most probable value is abnormally high [18] for these three series. The short alkyl chain probably changes the entropic effects, which is usually connected with the disordered movements of the alkyl and alkoxy chains.

Table 3. Temperatures (°C) and enthalpies (kJ·mol^{-1}) of the 4-propyl-4′-alkoxyazobenzenes. In square brackets enthalpy of the phase transition; in round brackets temperature of the monotropic phase transition.

m	Melting	Recrystallization	SmI		SmC		SmA		N		Izo
1	61.1 [52.93]	36.6 [50.44]							•	67.9 [1.56]	•
2	88.4 [52.15]	81.0 [56.73]							•	98.3 [2.74]	•
3	85.4 [53.64]	72.6 [58.67]									•
4	71.2 [41.11]	64.0 [42.73]							•	84.8 [2.64]	•
5	53.4 [35.02]	48.8 [36.76]							•	73.6 [2.96]	•
6	62.8 [64.52]	47.7 [56.05]							•	81.1 [3.01]	•
7	63.8 [90.71]	43.0 [84.33]							•	76.4 [2.70]	•
8	65.7 [94.93]	46.2 [76.54]			•	(47.3)	•	(52.3) [3.99]	•	81.0 [3.39]	•
9	63.0 [105.1]	50.8 [88.55]			•	(51.4)	•	(61.3) [4.27]	•	78.7 [3.64]	•
10	64.1 [91.25]	48.3 [76.69]	•	(50.5) [5.73]			•	68.7 [5.09]	•	80.8 [4.71]	•
11	70.7 [83.72]	50.2 [93.32]	•	(51.8) [6.24]			•	72.3 [5.57]	•	79.1 [4.79]	•
12	69.3 [105.3]	47.2 [82.82]	•	(59.4) [7.70]			•	77.1 [10.50]	•	80.8 [6.01]	•

Table 3 (continuation)

14	71.6 [113.7]	54.6 [96.89]	•	(65.4) [9.41]	•	79.5 [26.36]	•
16	73.9 [107.9]	50.9 [101.7]	•	(70.4) [11.56]	•	79.2 [26.92]	•
18	67.4 [82.54]	61.2 [81.34]					•

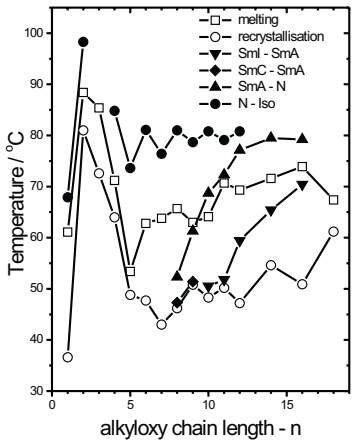


Figure 3. Phase diagram of the 4-propyl-4′-alkoxyazobenzenes.

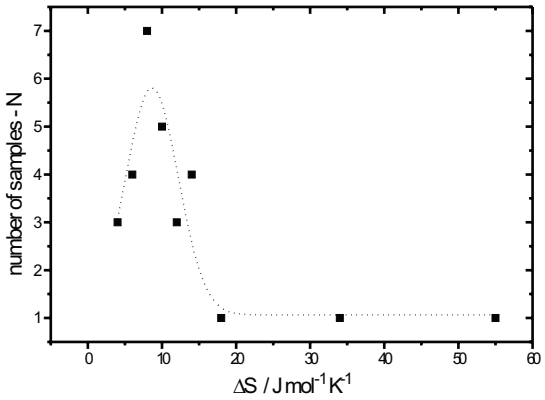


Figure 4. Statistics of the entropy values of the phase transition N-Iso.

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