Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Properties of 4-Alkoxy-4′- Chloroazobenzenes

Zbigniew Galewski [a]
[a] Institute of Chemistry, University of Wroclaw, 14, Joliot-Curie, 50-383, Wroclaw, Poland
Version of record first published: 04 Oct 2006.

To cite this article: Zbigniew Galewski (1995): Liquid Crystalline Properties of 4-Alkoxy-4′-Chloroazobenzenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 265:1, 77-87

To link to this article: http://dx.doi.org/10.1080/10587259508041680

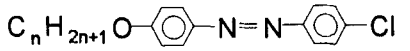
Mol. Cryst. Liq. Cryst. 1995, Vol. 265, pp. 77–87
Reprints available directly from the publisher
Photocopying permitted by license only

LIQUID CRYSTALLINE PROPERTIES OF 4-ALKOXY-4'-CHLOROAZOBENZENES

ZBIGNIEW GALEWSKI
Institute of Chemistry, University of Wrocław,
14, Joliot-Curie, 50-383 Wrocław, Poland.

Abstract

New family of liquid crystalline compounds with high dipole moment of the general formula:



has been synthesised. On the basis of texture observation, DTA calorimetry and thermooptics, smectic A, Smectic E and nematic phases were identified. The temperatures and enthalpies of phase transition are discussed and compared with the analogous Schiff base family, 4-chlorobenzylidene-4'alkoxyanilines.

INTRODUCTION

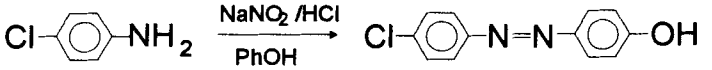
The azobenzene derivatives were among the first ten discovered liquid crystalline compounds [1,2]. In spite of that there were no detailed investigations of this kind of compounds. The alkoxy,4'-alkylazobenezens with short alkyl chains (until butoxy) were firstly described by Steinsträsser and Pohl in 1973 [3]. They recognised only nematic mesophases. de Jeu in the series of papers [4,5,6] presents liquid crystalline properties and their physical properties of 4-alkoxy,4'-butylazobenzenes. The family with longer alkyl chains was investigated by the Halle group for 4-alkoxy,4'-nonylazobenzenes [7]. On the base of X-ray diffraction, texture observations and DSC calorimetry smectic A, smectic C, smectic I and smectic G were identified.

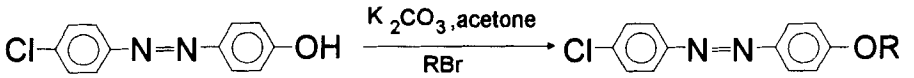
Dąbrowski [8,9] described the families with both alkyl chains (one chain was methyl and ethyl). They found very low melting temperatures and only nematic mesophase.
For application important are compounds with high dielectric anisotropy. Among them there were only compounds with cyano [10,11,12,13] and nitro group [14,15] described. The azobenzene compounds are very easy in preparation and purification and have rich polymorphism [16,17]. The disadvantage is their yellow colour and the UV and Vis instability. Very recently [18] they were successfully applied in non-linear optics.

The main aim of this paper is the presentation of the new family of azobenzenes liquid crystalline compounds with the chloro group. Their properties are compared with the analogue Schiff base 4-chlorobenzylidene,4'-alkoxyanilines.

SYNTHESIS

The main root of preparations of 4-alkoxy,4'-chloroazobenzenes is as follows:

1. 

2. 

The both steps of synthesis were done with the standard method [19]. All compounds were crystallised from ethanol end next purified by column chromatography. Silica gel (Merck Kiesielgel 60) with chloroform as an eluent was used. The purity was proven by TLC, NMR spectroscopy and elemental analysis.

For phase transition investigation all compounds were melted under high vacuum for solvent removing. Table 1 presents elemental analysis results:

TABLE 1. Elemental Analysis of 4-alkoxy,4'-chloroazobenzenes.

	calculated			found		
n	C	H	N	C	H	N
1	63.3	4.49	11.4	63.18	4.36	11.32
2	64.5	5.03	10.7	64.93	5.34	10.31
3	65.6	5.50	10.2	65.41	5.36	10.18
4	66.5	5.93	9.70	66.55	5.77	9.72
5	67.4	6.32	9.25	67.27	6.21	9.25
6	68.2	6.68	8.84	68.01	6.59	8.83
7	69.0	7.01	8.47	69.18	7.01	8.49
8	69.7	7.31	8.12	69.82	7.31	8.12
9	70.3	7.58	7.81	70.07	7.62	7.68
10	70.9	7.84	7.51	70.42	7.70	7.41
11	71.4	8.07	7.24	71.20	8.07	7.15
12	71.9	8.29	6.99	71.70	8.26	7.02

EXPERIMENTAL

Thermo-optics set-up was described in the other paper [20]. Calorimetric measurements were performed with a Rigaku DSC unit and DTA set-up made by UNIPAN (Fig.1). In the last one all voltage signals were measured by two digital multimeters (Meratronik V542.1 and Black Star 4503), which through the IEC625 bus were connected to the IBM 386DX computer. Heat effect was numerically calculated using as a standard five organic compounds with known melting enthalpy [21]. Results of measurements are presented in Table 2. (ΔH in kJ/mol in square brackets)

Photographs were done with the help of a Pentacon camera connected to the AMPLIVAPOL microscope.

RESULTS

The temperatures of the phase transitions were detected from TOA, which was found as most accurate (possible 0.1 K precession).

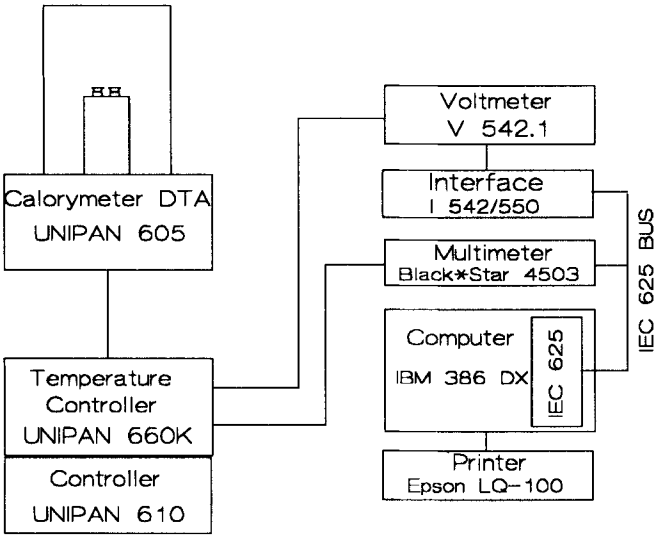


Fig.1. Experimental arrangement for DTA measurements.

TABLE 2. Phase transition temperatures of 4-alkoxy,4'-chloroazobenzenes.

	Cr	S_E	S_X	S_A	N	I
1	• 119.6 [37.0]					•
2	• 101.8 [31.3]					•
3	• 102.6 [35.5]					•
4	• 91.8 [35.1]				• (86.8) [3.2]	•
5	• 81.0 [31.1]	• (71.0) [4.10]	• (74.0) [1.1]	• 86.5 [8.1]		•
6	• 85.1 [34.6]			• 91.0 [7.9]		•
7	• 84.4 [41.5]		• (69.0) [1.0]	• 92.0 [9.3]		•
8	• 79.6 [82.2]			• 94.6 [12.9]		•
9	• 84.0 [60.6]			• 95.0 [6.9]		•
10	• 83.6 60.1]			• 96.0 [7.4]		•
11	• 93.5 [114.]			• 94.7 [13.6]		•
12	• 85.0 [61.3]			• 93.3 [8.8]		•

First member of the investigated family with liquid crystalline properties was butoxy derivative. On the base of DTA and thermo-optics scans (Fig.2) and the texture investigation (Fig.7) there was identified only monotropic nematic.
The pentyl derivative shows very interesting polymorphism. The DTA scans see three mesophases, but TOA only two (Fig.3) which were identified as a smectic A and smectic E (Fig.8,9) [23,24]. The same situation, one extra phase not visible in TOA, has been found in the heptyl derivative (Fig 4.)

All other compounds have only one smectic A mesophase. Typical for them are two pics in DTA and two discontinuity in TOA. (Fig.5). They have characteristic texture, focal conics (Fig.10), typical for smectics A. Full phase diagram is presented in Fig 6.

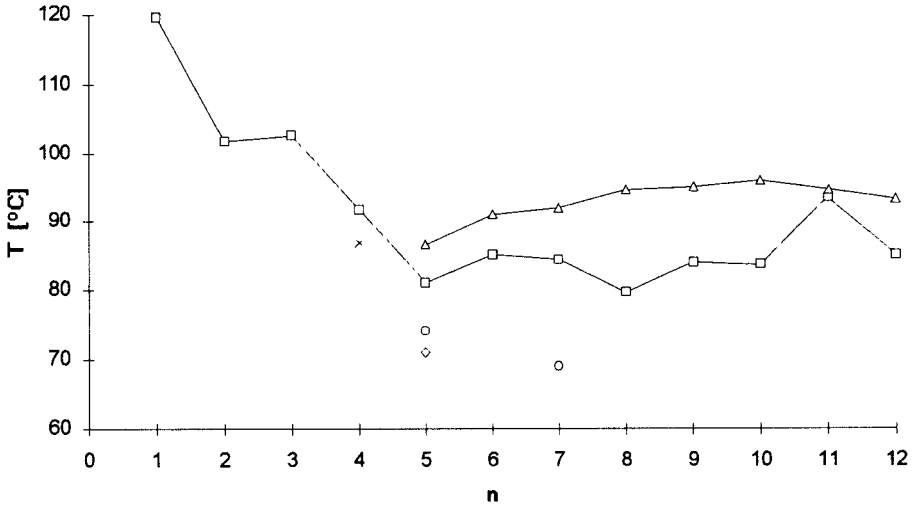


Fig.6. Phase diagramme of 4-chloro,4'-alkoxyazobenzens: □- melting, △- $S_A \rightarrow$Iso, x- N→Iso, ◊ - $S_X \rightarrow S_E$, ○ - $S_A \rightarrow S_X$.

The phase situation is similar to an analogous family, 4-chlorobenzylidene,4'-alkoxyanilines [24]. The difference is only in one atom in the central group. Such small change does not change the lattice energy. There are the same ranges of melting temperatures and the mesomorphism firstly apears in the butoxy derivatives. The phase situation is different. Schiff bases have two smectics modifications A and B, but azo family has only one, smectic A. In butoxy derivative there is monotropic nematic phase, not existing in the Schiff base. The pentyloxy, azo compound has extra smectic E.

ACKNOWLEDGMENTS

The author wishes to thank Prof. L.Sobczyk for his interest in this work and Mr J.Zienkiewicz for his technical assistance.

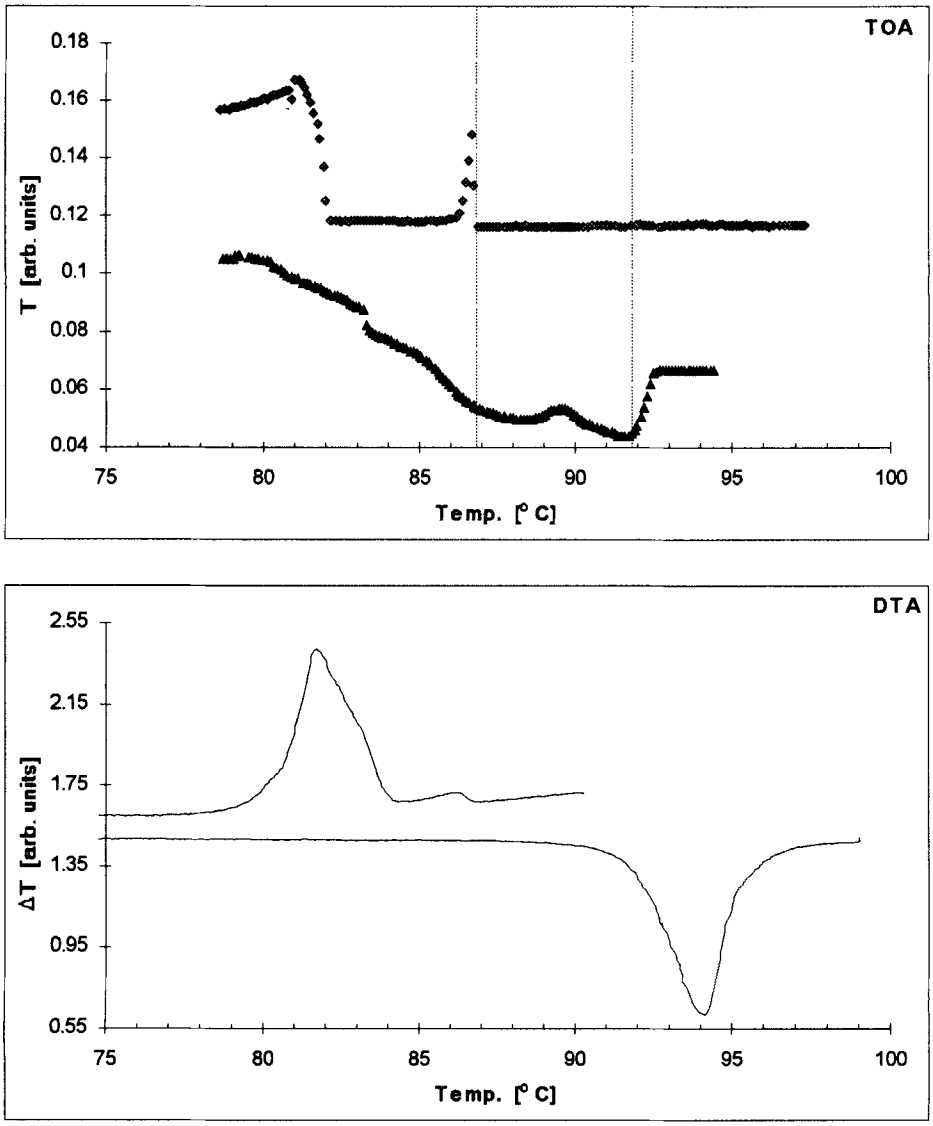


Fig.2. TOA and DTA scans for 4-butoxy,4'-chloroazobenze

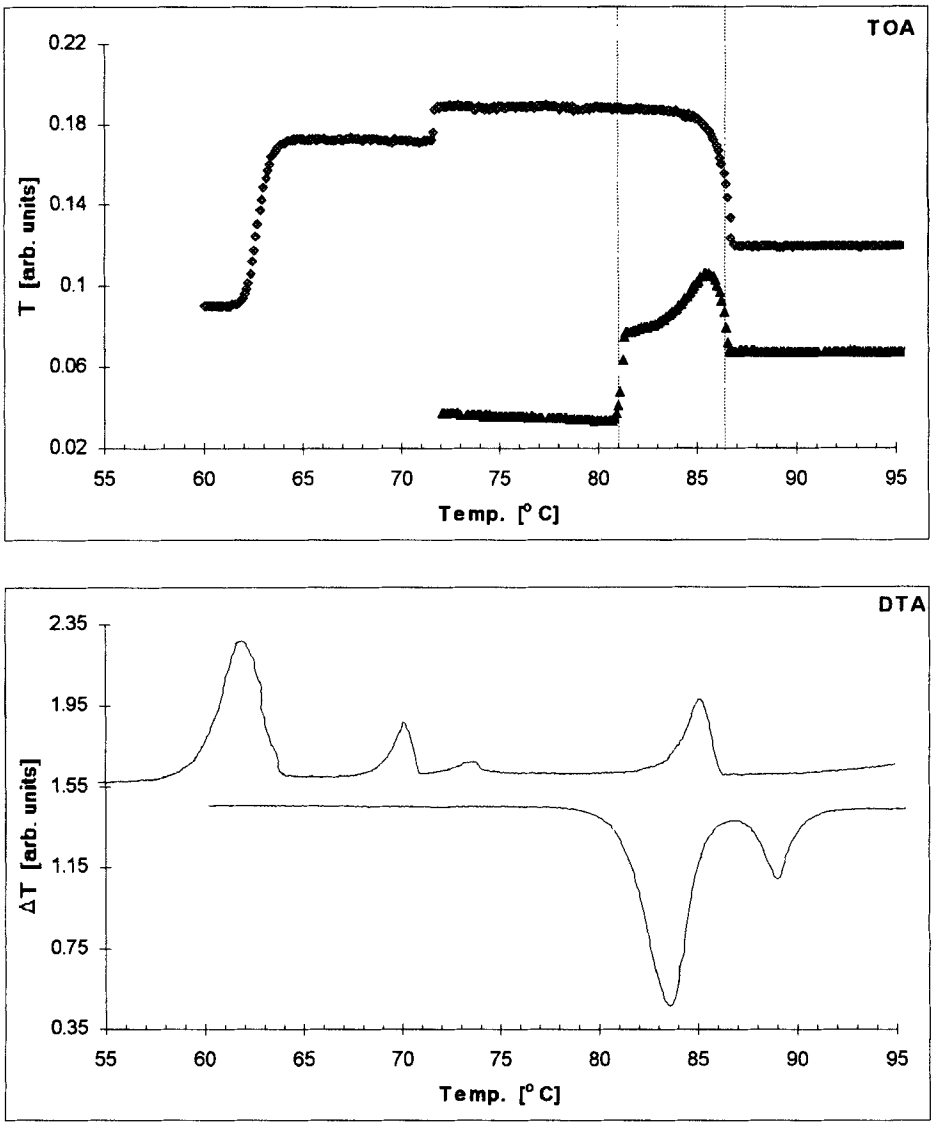


Fig.3. TOA and DTA scans for 4-pentyloxy,4'-chloroazobenze

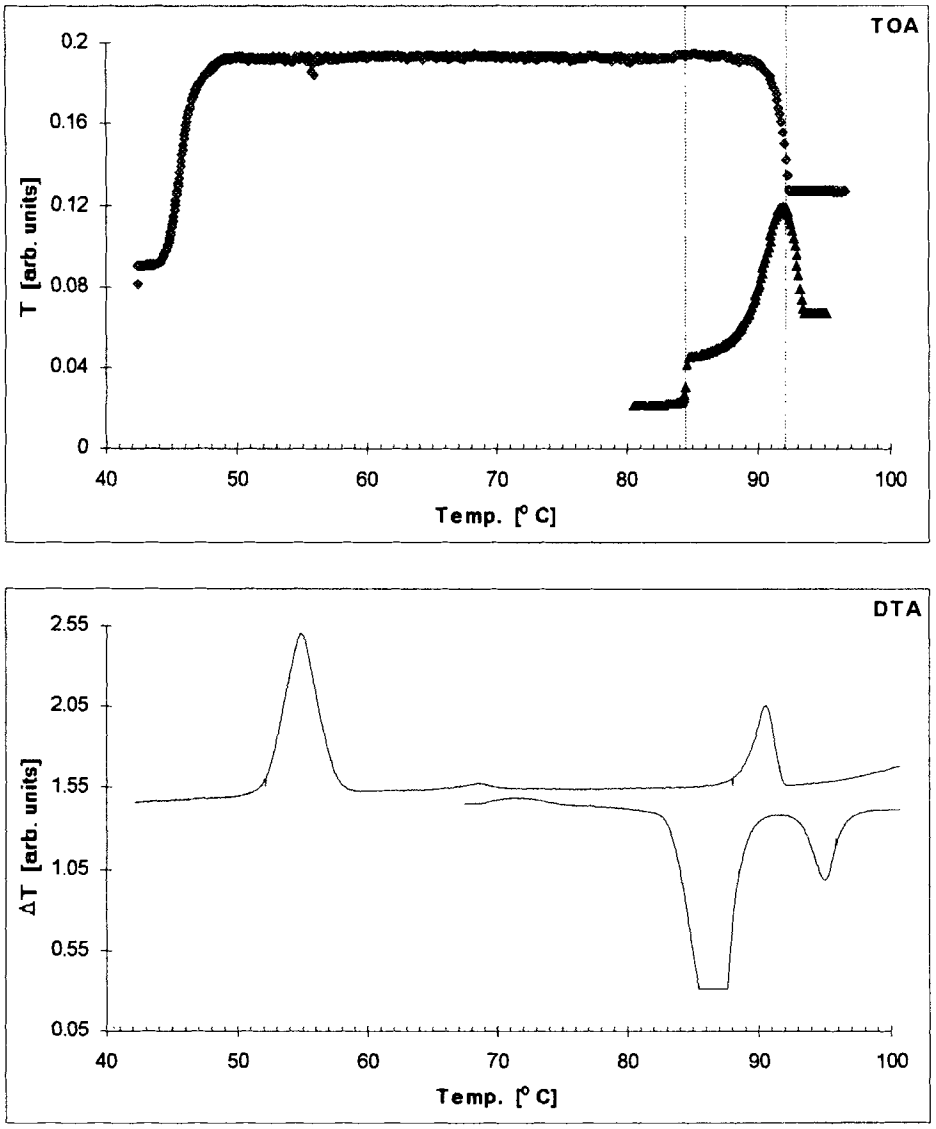


Fig.4. TOA and DTA scans for 4-heptyloxy,4'-chloroazobenze

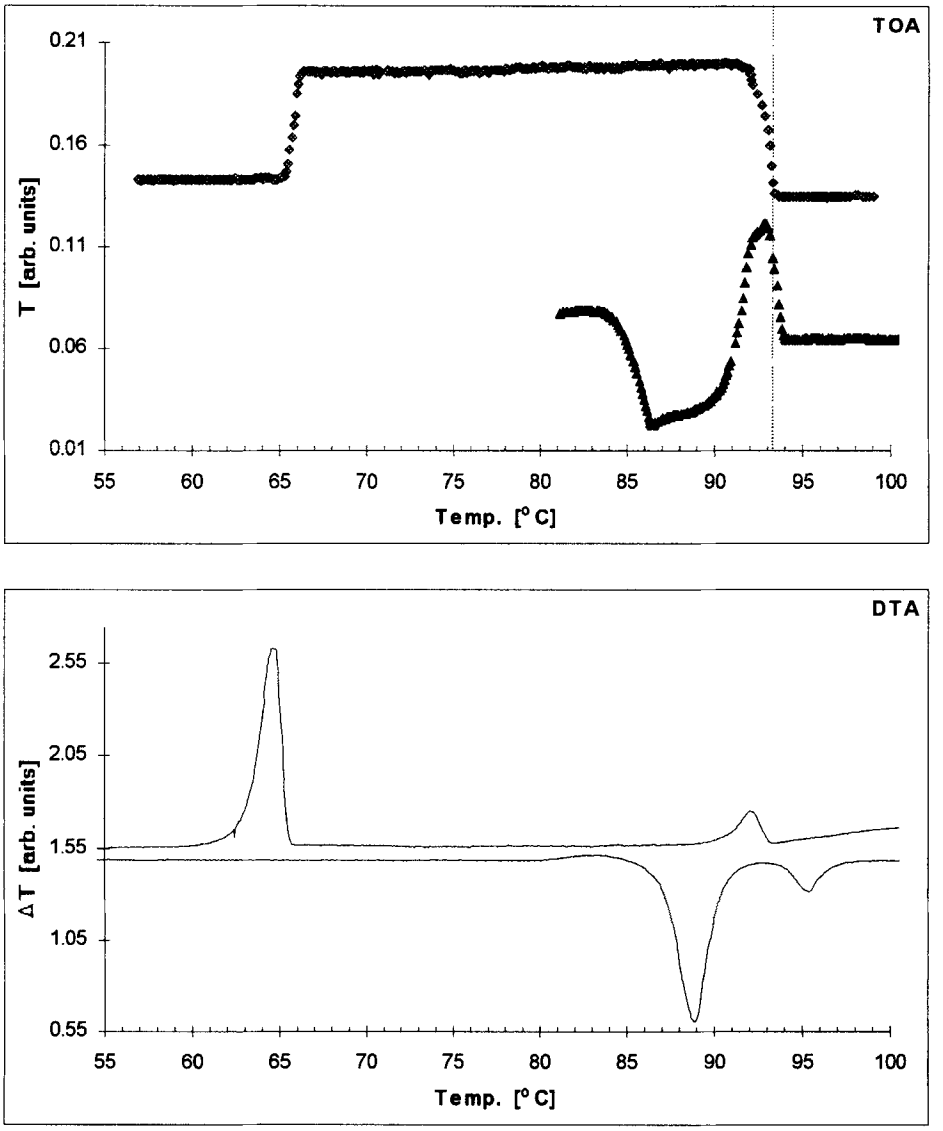


Fig.5. TOA and DTA scans for 4-dodecyloxy,4'-chloroazobenze

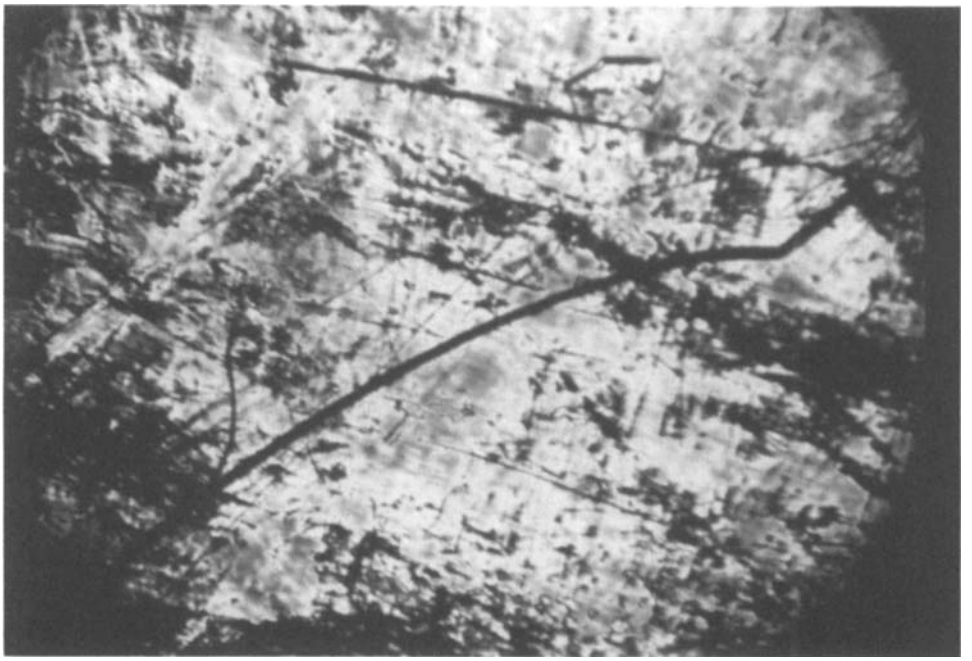


Fig.7. 4-butoxy,4'-chloroazobenzene, T=84°C, marble texture. See Color Plate V.

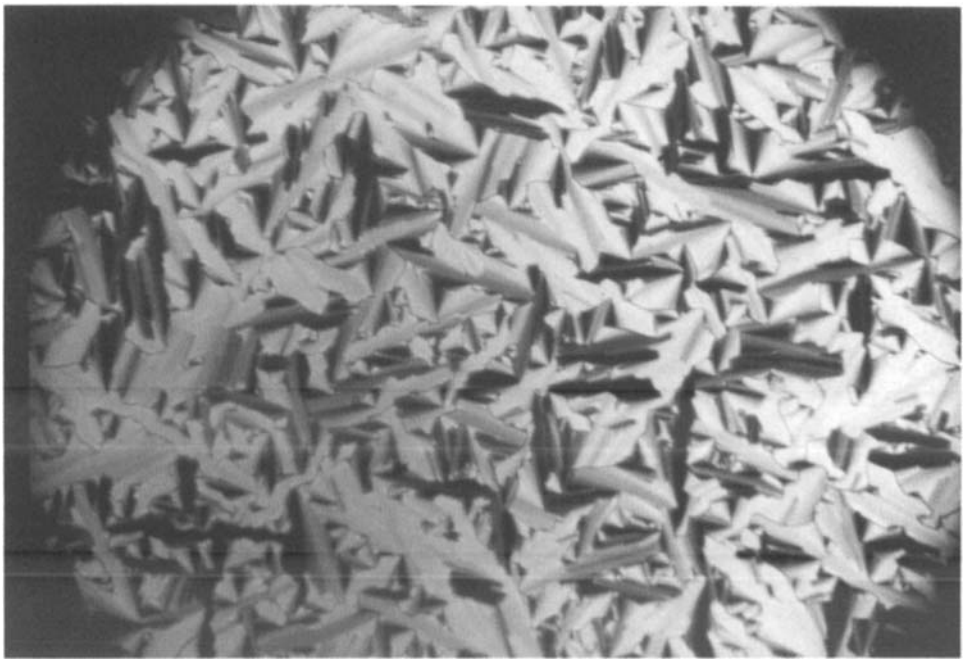


Fig.8. 4-pentyloxy,4'-chloroazobenzene, T=80°C, smectic A. See Color Plate VI.

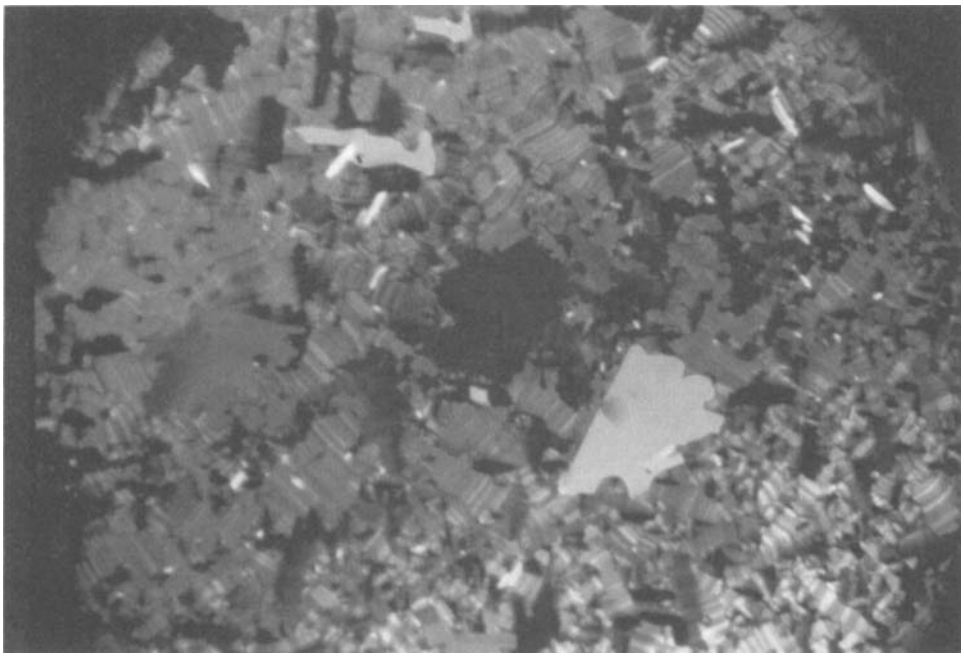


Fig.9. 4-pentyloxy,4'-chloroazobenzene, T=68°C, smectic E . See Color Plate VII.

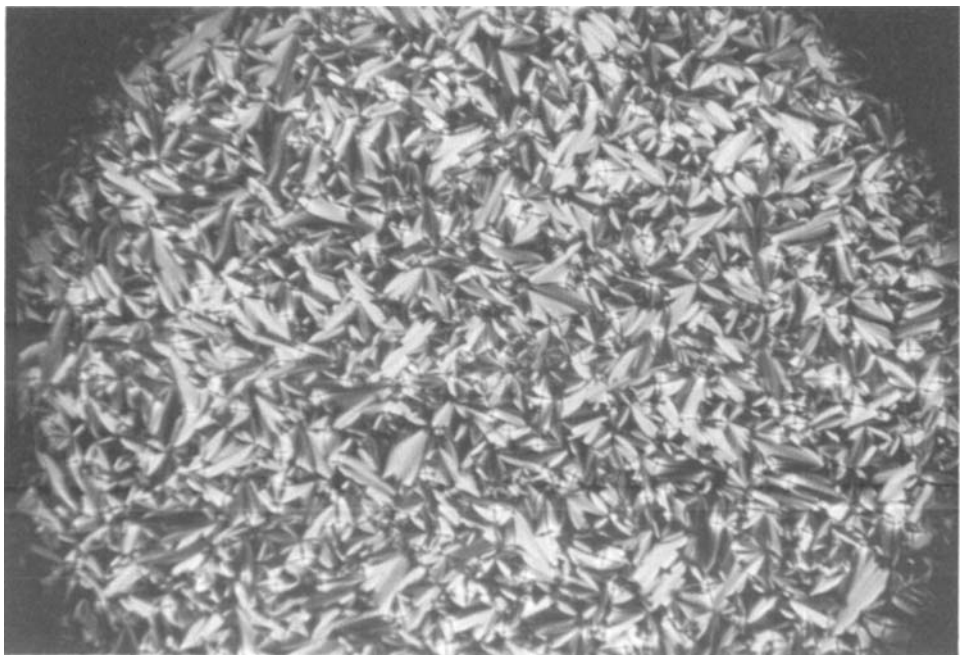


Fig.10. 4-heptyloxy,4'-chloroazobenzene, T=89°C, smectic A. See Color Plate VIII.

REFERENCES

1. T.Rotarski, Ber. 36, 3158(1903).
2. O.Lehmann, Ann Phys. 21, 181(1906).
3. R.Steisträsser & L.Pohl, Z.Natuforsch. 26b, 577(1971).
4. W.H.de Jeu & J.Vander Veen, Philips Res.Repts 27,172(1972).
5. W.H.de Jeu ,J.Vander Veen & W.J.A.Goosens, Solid State Comm. 12, 405(1973).
6. W.H.de Jeu & J.Vander Veen, Philips Tech. Rev. 37,131(1977).
7. G.Pelz,N.K.Sharma,L.Richter,A.Wiegeleben,G.Schröder,S.Dick,D.Demus, Z.Phys.Chem. Leipzig 262, 2(1981).
8. R.Dąbrowski, K.Kenig,Z.Raszewski,J.Kędzierski, Mol.Cryst.Liq.Cryst. 61, 131(1980).
9. R.Dąbrowski, K.Kenig,Z.Raszewski,J.Kędzierski, Biuletyn WAT, 39, 79(1980).
10. R.Dąbrowski, G.Adamska, Z.Stolarzowa, A.Konarzewski, W.Wacławek, Pol.J.Chem. 54, 1233(1980).
11. R.Dąbrowski,S.Dwojacki,M.Miłowski,Biuletyn WAT, 29,29(1980).
12. V.T.Lazareva,V.V.Titov,K.V.Rothman, Zh.Org.Khim. 12, 149(1976).
13. J.Van der Veen,T.G.J.M.Hegge, Angew.Chem. 86, 378(1974).
14. R.Dąbrowski, Z.Rzepka, Biuletyn WAT 31, 63(1982).
15. Mei-Sing Ho, B.M.Fung,J.P.Bayle, Mol.Cryst.Liq.Cryst. 225, 383(1993).
16. D.Demus,H.Demus,H.Zaschke, Flüssige Kristalle in Tabellen (VEB Deutscher Verlag für Grundstoffindustrie,Leipzig,1974).
17. D.Demus,H.Zaschke, Flüssige Kristalle in Tabellen II (VEB Deutscher Verlag für Grundstoffindustrie,Leipzig,1984).
18. C.B.McArdle ed., Side Chain liquid Crystalline Polymers, (Blackie,Glasgow & London,1989).
19. Vogel's Handbook of Practical Organic Chemistry, (longman Group Limited, London,1978, IV-th edition.
20. Z.Galewski, J.Zienkiewicz , in preparation.
21. W.E.Acree Jr. Thermochim Acta, 189, 37(1991).
22. G.W.Goodby & J.W.Gray, Smectic Liquid Crystals, (leonard Hill, Glasgow,1984).
23. D.Demus,L.Richter, Textures of liquid Crystals, (VEB Deutscher Verlag für Grundstoffindustrie,Leipzig,1978).
24. Z.Galewski,H.J.Coles, in preparation.