Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis and Some Physical Properties of Unsymmetrical 4,4′-Dialkylazoxybenzenes

R. Dabrowski [a] , K. Kenig [a] , Z. Raszewski [a] , J. Kedzierski [a] & K. Sadowska [b]

[a] Military Technical Academy, 00-908, Warsaw, Poland

[b] Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224, Warsaw, Poland

Version of record first published: 20 Apr 2011.

To cite this article: R. Dabrowski , K. Kenig , Z. Raszewski , J. Kedzierski & K. Sadowska (1980): Synthesis and Some Physical Properties of Unsymmetrical 4,4′-Dialkylazoxybenzenes, Molecular Crystals and Liquid Crystals, 61:1-2, 61-78

To link to this article: http://dx.doi.org/10.1080/00268948008081984

Mol. Cryst. Liq. Cryst., 1980, Vol. 61, pp. 61–78
0026-8941/80/6102-0061$04.50/0

Synthesis and Some Physical Properties of Unsymmetrical 4,4′-Dialkylazoxybenzenes

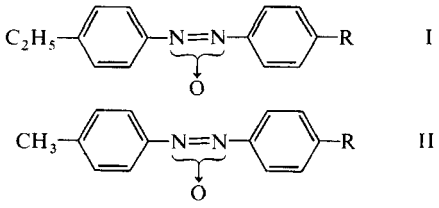
R. DABROWSKI, K. KENIG, Z. RASZEWSKI, and J. KEDZIERSKI
Military Technical Academy, 00-908 Warsaw, Poland.

and

K. SADOWSKA
Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland.

(*Received December 14, 1979*)

Two series of unsymmetrical 4,4′-dialkylazoxy compounds:



have been obtained, where R = C_mH_{2m+1} with m = 2 to 10. The method of their synthesis and the results of measurements of the phase transition temperatures, dielectric constants, refractive indices and densities are presented. Compounds I and in a lesser degree compounds II are low-melting nematics with a small positive anisotropy of the dielectric constant. In both series a strong alteration was observed of clearing point, dielectric constant anisotropy $\Delta\varepsilon$ and birefringence Δn with the number in of carbon atoms in the alkyl radical.

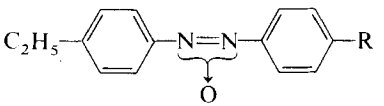
INTRODUCTION

It is desirable that the phase transition temperature from the solid to liquid-crystalline state be low in liquid crystals, since then they are most useful as displays or as solvents for NMR or ESR spectroscopy. So far only few compounds with mesogenic properties at temperatures close to 20° are known;

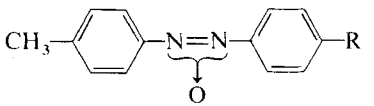
some examples are given in the works.[1–11] In all known low-melting mesogenic compounds the alkyl group is at least one of terminal substituents. Compounds with two alkyl substituents have the lowest melting temperatures when the substituents are of different length.[4]

The deficiency of low-melting mesogenic compounds is overcome by using composed of several compounds. Low-melting eutectic systems are easiest to obtain when both components are low-melting compounds. When seeking liquid crystals in which the mesophase would begin below room temperature, we assumed that 4,4′-dialkylazoxybenzenes should reveal such properties.

The azoxy group as the bridge connecting the benzene rings allows us to obtain compounds with higher clearing points as compared with the azo, azomethin or ester groups. Also asymmetry of substitution contributes to the lowering of the melting point. We checked that concept in an earlier work[12] by testing several compounds belonging to the 4-ethyl-4′-alkylazoxybenzene



I



II

where $R = C_mH_{2m+1}$ with $m = 2$ to 10, homologous series (formula I). In the present work additional compounds belonging to that series are described, as well as those belonging to the 4-methyl-4′-alkylazoxybenzene homologous series (formula II). We studied such physical properties of both series such as the phase transition temperatures, dielectric constants, refractive indices and densities in the liquid-crystalline and isotropic phases.

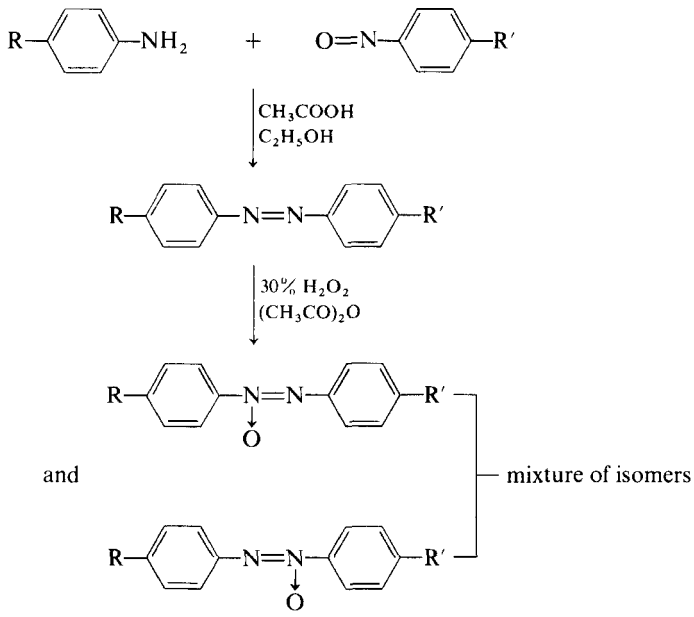
The compounds of the first homologous series have the ethyl group as permanent terminal substituent and an alkyl ($R = C_mH_{2m+1}$) with 2 to 10 carbon atoms as the variable substituent. In the second homologous series the methyl group is the permanent terminal substituent and the variable alkyl group is the same as in the first series.

EXPERIMENTAL

Preparation of materials

There are many methods of preparing azoxy compounds,[13] however, for obtaining unsymmetrically substituted compound of I and II types we can

use in fact only the following reaction scheme:



We used *p*-nitrosotoluene or *p*-nitrosoethylbenzene as one of the substrates since they are easily obtained from commercially available *p*-nitrotoluene or *p*-nitroethylbenzene according to procedure described by Murase[9] or in our work.[12] As second substrate we used *p*-*n*-alkylanilines obtained from *p*-*n*-alkylacetophenones in the Schmidt reaction.[14] The condensation of *p*-nitrosotoluene or *p*-nitrosoethylbenzene and *p*-*n*-alkylanilines proceeds readily with a good yield at room or somewhat higher temperature.

4-Ethyl-4′-alkylazobenzenes readily oxidize when heated at 80° with hydrogen peroxide in acetic acid. In distinction, 4-methyl-4′-alkylazobenzenes oxidize sparingly, so even heating for several dozens of hours under the above conditions does not lead to their complete oxidation. However, the time of oxydation is significantly reduced when benzene is present in the reaction medium. The experimental procedure will be illustrated for this case by a representative example:

4-methyl-4′-nonylazobenzene To 79.9 g (0.36 mole) of 4-*n*-nonylaniline in 200 ml of acetic acid 44 g (0.36 mole) of 4-nitrosotoluene in 150 ml of ethanol were added dropwise at 10°. The combined solutions were heated for 2 hours at 55°, then cooled and the product formed was filtered off, twice crystallized from a 2 : 1 methanol-acetone mixture. We obtained 70 g of the orange product (yield 60%) with melting range 55.5–56.0°. IR (KBr pellet) 1150 cm^{-1}

(Ph—N=); electron spectrum in hexane: λ_{max} 435 nm, log ε = 3.02, $n \rightarrow \pi$ band of the chromophore —N=N—. Anal. calcd. for $C_{22}H_{30}N_2$: C = 81.93%, H = 9.39%, N = 8.69%; Found: C = 82.21%, H = 9.33%, N = 8.74%.

4-methyl-4′-nonylazoxybenzene A 67.5 g portion of the above obtained 4-methyl-4′-*n*-nonylazobenzene was dissolved in 120 ml of benzene, heated to 75°, when a solution of peracetic acid obtained from 950 ml of acetic anhydride and 215 ml of 30% hydrogen peroxide was added dropwise. The reaction mixture was further heated until the solution turned yellow, which took about 6 hours. After cooling the contents were diluted with water, and 400 ml of benzene were added. The benzene layer was separated, washed successively with water, 2% NaOH and water again, and dried over anhydrous $MgSO_4$. Then benzene was distilled off and the oily residue was dissolved in *n*-hexane and filtered through a 7 cm layer of silica gel. *n*-Hexane was removed and the product was twice crystallized from methanol. We obtained 63 g (yield 90%) of 4-methyl-4′-nonylazoxybenzene with melting range 34.5–35.5° and clearing point 60°; IR 915 cm^{-1} (=N $\rightarrow$ O), 1165 cm^{-1} (Ph—N=), 1330 cm^{-1} (—N=N—). Anal. calcd. for:

$C_{22}H_{30}N_2O$: C = 78.05%, H = 8.94%, N = 8.27%;

Found: C – 77.96%, H = 9.08%, N = 8.33%.

Measurements of the phase transition temperatures, dielectric constants, refractive indices and densities

The phase transition temperatures were determined using the PHMK Analytik (Dresden) or Reichert polarizing microscope with a cooled and heated stage. The tested compound was placed between glass plates. The smectic phase was identified by comparing the texture and testing the miscibility with 4,4′-diheptylazoxybenzene which is a S_A smectic.[15]

The static dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_i were measured in dependence on temperature by means of a precision Tesla BM 484 bridge with inner frequency of 1592 Hz. The parallel condenser plates with brass electrodes separated by a Teflon liner 0.22 mm thick served as container for the specimen. A magnetic ordering field of 1T induction and a measuring electric field of 3V were used. The temperature was measured by means of differential copper-constantan thermocouple calibrated under the working conditions. More details about the measuring cell, apparatus and measuring technique can be found in the works.[16,17]

The refractive index in the isotropic phase n_i and the main refractive indices n_0 and n_e in the nematic phase were measured with Abbe's refract-

ometer for light of wavelength $\lambda = 589.3$ nm. The measuring prisms were thermostated with an accuracy of 0.1°. The limiting line was observed in the refractometer using a polarizer. Ordering of the nematic layer with respect to the surface of the measuring prism was achieved by rubbing. The measurement error was ± 0.0002 for n_i and ± 0.0005 for n_0 and n_e. More details on the measuring technique are to be found in work.[18,19]

The density of the compounds was measured in the liquid crystalline and isotropic phases with a pycnometer of 6.66 ml volume. The thermostating accuracy up to 35° was ±0.02° and above 35° ± 0.03°.

RESULTS

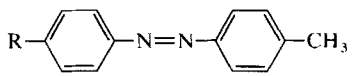
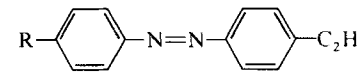
Mesomorphic properties

4-Methyl-4'-alkylazobenzenes have comparatively high melting temperatures and crystallize readily, so it was not possible to overcool them to lower temperatures. Only compounds with the heptyl and higher alkyl substituents could be overcooled for a short time, which allowed us to find that they have a monotropic nematic phase. In the remaining compounds we did not manage to observe that phase (Table I).

High melting temperatures are characteristic of the majority of compounds with the methyl group as terminal substituent even if the other terminal substituent is a longer alkyl or alkoxy group.[20]

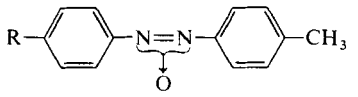
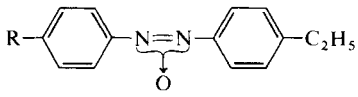
4-Ethyl-4'-alkylazobenzenes have starting with $R = C_4H_9$ low melting temperatures, depending but slightly on the length of R (Table I). For the compound with heptyl substituent, which reveals the lowest melting point

TABLE I

				
R	m.p. (°C)	N → I (°C)	m.p. (°C)	N → I (°C)
CH_3	143.0 – 144		77.5 – 78	
C_2H_5	77.5 – 78		62.5 – 63	
C_3H_7	60.5 – 61		44.0 – 44.5	
C_4H_9	53.5 – 54		22.5 – 23	
C_5H_{11}	65.0 – 65.5		25.5 – 26	10 mon
C_6H_{13}	60.0 – 60.5		22.5 – 23	
C_7H_{15}	52.5 – 53	24.5 mon	18.0	29.5
C_8H_{17}	53.5 – 54	21.0 mon	25.5 – 26	18 mon
C_9H_{19}	55.5 – 56.0	32.0 mon	30.0 – 30.5	25 mon
$C_{10}H_{21}$	57.0 – 57.5	29.0 mon	37.0 – 37.5	27 mon

N = nematic; mon = monotropic.

TABLE II

R	m.p. (°C)	S → N (°C)	N → I (°C)	m.p. (°C)	S → N (°C)	N → I (°C)
CH_3	70		38 mon 69.8x	40 – 47		31 mon
C_2H_5	40 – 47		31 mon	23 – 23.5		0 mom
C_3H_7	6 – 7		50.5 mon	13.5 – 14		33
C_4H_9	24.5 – 27		28.5	16.5		12 mon
C_5H_{11}	18 – 22.5		53.5	5		40.5
C_6H_{13}	24.5 – 25.5		42.5	9.5		31.5
C_7H_{15}	31 – 32		56	8		45
C_8H_{17}	26 – 27.5		51	10.5	2 mon	42
C_9H_{19}	34.5 – 35.5		60	19.7	23	49.5
$C_{10}H_{21}$	32 – 34	25.5 mon	57.5	24.0	26.5	47.5

S = smectic; N = nematic; mon = monotropic; x = Ref. (22).

in this series, we observed the enantiotropic liquid-crystalline phase, though in the range of about 1° only. The successive compounds in this series have a monotropic nematic phase only.

4-Ethyl- and 4-methyl-4′-alkylazoxybenzenes are in their great majority, as distinguished from the azo compounds, enantiotropic mesogens, and their nematic phase exists in a wide range of temperatures (Table II). In both series the clearing points increase with the length of the alkyl substituent. The unsymmetrically substituted 4-ethyl-4′-alkylazoxybenzenes (Figure 1b) show clearing points by about 20° lower than the symmetric 4,4′-dialkylazoxybenzenes (Figure 1a) described by van der Veen and de Jeu.[14] Their melting temperatures are also lower by the same value owing to which the range of their mesophase is almost as wide as that of the symmetric compounds. Several of them melt in the range 5–10°, whereas in symmetrically substituted compounds only the butyl and pentyl derivatives are liquid below 25°.

The low melting points of 4-ethyl-4′-alkylazoxybenzenes can only in part be attributed to the fact that those compounds are composed of two-position isomers. In our opinion this is also largely due to the presence of the ethyl group as terminal substituent which contributes in this case very advantageously to the lowering of the melting point. The symmetric 4,4′-diethylazoxybenzene, in which position isomerism does not occur, melts at 23°. However, the latter melting temperature is much lower than that of the compounds preceding and following that substance in the homologous series.

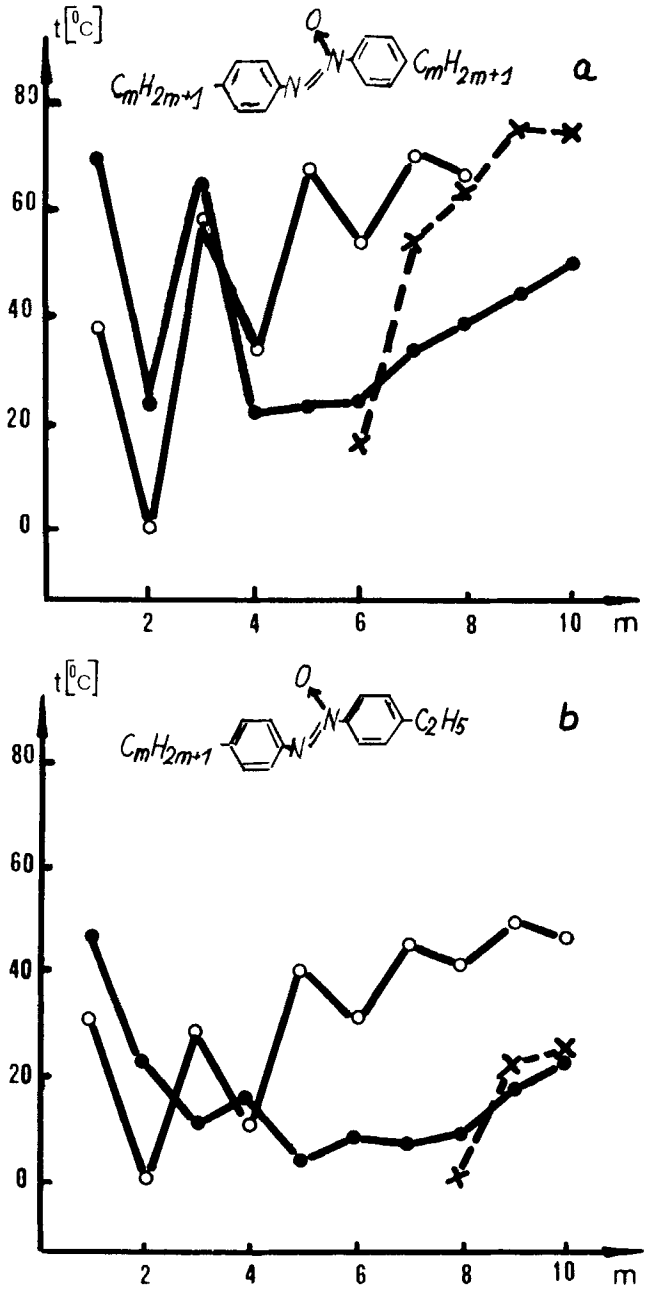


FIGURE 1 The phase transition temperatures in the three homologous series of dialkyl azoxybenzene derivatives: ○ = clearing point, ● = melting point, × = smectic-nematic or smectic-isotropic phase transition points; (a)—phase transitions after Ref. (11) with the exception of the results for $m = 1$ and 2.

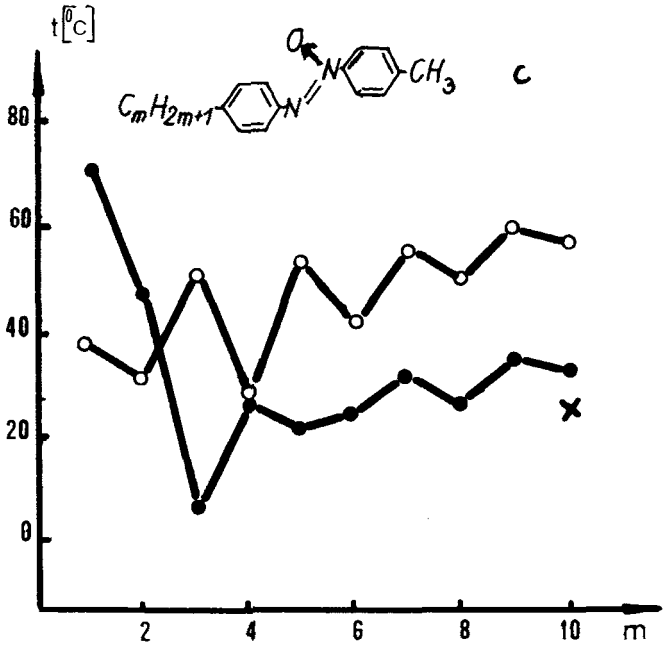


FIGURE 1 (*continued*) The phase transition temperatures in the three homologous series of dialkyl azoxybenzene derivatives: ○ = clearing point, ● = melting point, × = smectic-nematic or smectic-isotropic phase transition points; (a)—phase transitions after Ref. (11) with the exception of the results for $m = 1$ and 2.

The transformation of the azo bridge in the symmetric 4,4′-dialkylazobenzenes to the azoxy bridge results in the lowering of the melting point.[21] Considering the above fact and that most 4-ethyl-4′-alkylazobenzenes melt at about 20° we can expect that the melting points of pure 4-ethyl-4′-alkylazoxy compound position isomers with a pentyl, hexyl, heptyl or octyl radical will be lower than 20°.

4-Methyl-4′-alkylazoxybenzenes melt at temperatures about 10–15° higher than the compounds with the ethyl substituent with the exception of 4-methyl-4′-propylazoxybenzene which melts abnormally low, i.e. at 7° (Table II).

The disadvantageous increase of the melting point of compounds with the methyl group is advantageously compensated by their higher clearing points.

The liquid-crystalline properties of 4,4′-dimethylazoxybenzene, which is at the same time the first compound of all the homologous series of azoxy compounds discussed here, require some comment. That compound was studied by Campbell and Henderson,[22] who report that it is a monotropic

nematic with a clearing point of 69.2° (m.p. 70°). During slow cooling of the molten compound they observed the formation of areas of liquid crystal in which laths of solid start to grow. We found that was not a real liquid-crystalline state but some intermediate phase characterized by strong birefringence which by its behaviour reminds the liquid-crystalline state. This intermediary phase can be observed both during the melting of 4,4′-dimethylazoxybenzene and directly before crystallization. Similar properties are revealed by stilbene as reported by Kurik.[23] The normal nematic phase appears in 4,4′-dimethylazoxybenzene at 38°. We determined it basing on the clearing points of the two-component systems: 4-methyl-4′-butylazoxybenzene-4,4′-dimethylazoxybenzene and 4-methyl-4′-propylazoxybenzene-4,4′-dimethylazoxybenzene. In the former system the clearing point rises and in the latter it decreases with the amount of 4,4′-dimethylazoxybenzene present. The clearing points of pure 4-methyl-4′-butylazoxybenzene and 4-methyl-4′-propylazoxybenzene are 28.5° and 50.5°, respectively.

Both series of the unsymmetrical 4,4′-dialkylazoxybenzenes (I and II) presented here reveal a less pronounced smectogenic behaviour (Figure 1a, 1b and 1c) than the symmetric ones. In 4-ethyl-4′-alkylazoxybenzenes the smectic phase S_A was observed for compounds with nonyl and decyl radicals but only in a small range of temperatures (2–3° above the m.p.); the compound with the octyl radical has only a monotropic smectic phase.

In 4-methyl-4′-alkylazoxybenzenes we observed only monotropic smectic phase for compound with decyl radical. As distinguished from the above considered compounds, 4,4′-diheptylazoxybenzene has a smectic phase S_A 20° above the m.p. (Figure 1a). It can be believed therefore that the smectogenic behaviour of dialkylazoxy compounds depends not so much on the length of one of the terminal substituents as on the total length and number of atoms in both terminal substituents. This is observed when the total number of carbon atoms in both substituents exceeds 10. The total length of the alkyl chains determines the dispersive forces and the molecular weight. Both these factors affect significantly the translational displacement ability of the particular molecules. 4-Ethyl- and 4-methyl-4′-alkylazoxybenzenes seem to be, owing to their low melting points and small tendency to form smectic phases, particularly suitable as components for preparing mixtures liquid at low temperatures. They also seem to be a convenient model of a nematic whose structure is nearest to ideal.

Physical properties

Refractive indeces The temperature dependence of the refractive indeces in the isotropic phase n_i for the ordinary n_0 and extraordinary n_e rays for compounds of series I and II is similar to those observed for symmetric

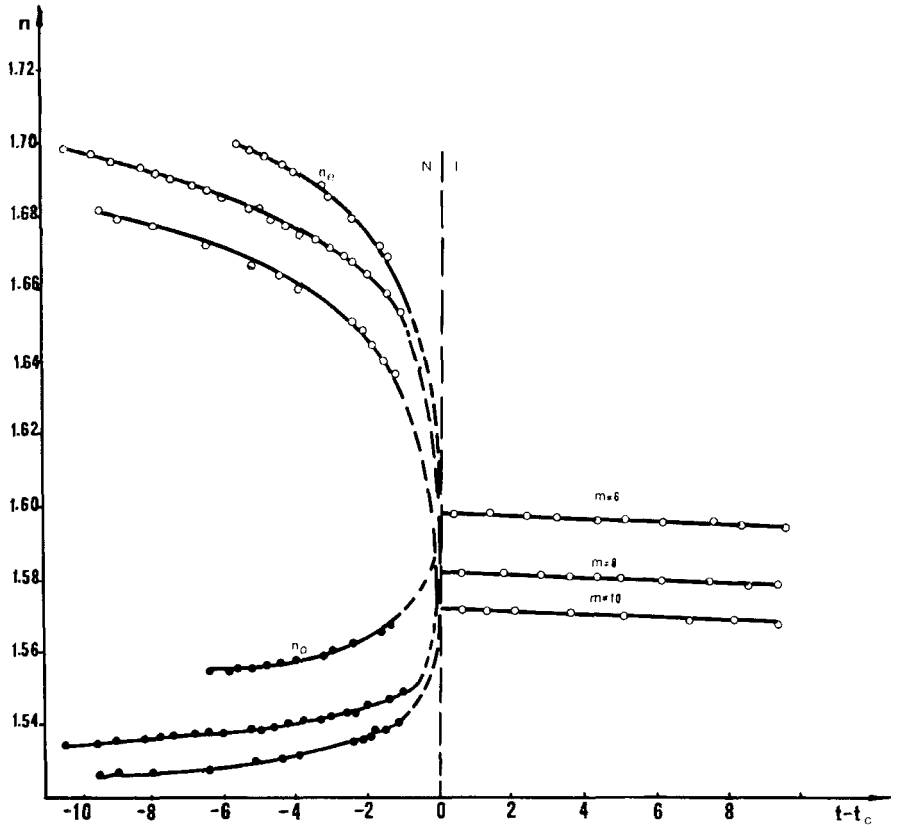


FIGURE 2 Variation of the refractive indeces in the isotropic and nematic phases with temperature (n_0 and n_e refer to the ordinary and extraordinary rays, respectively) for three compounds belonging to the 4-ethyl-4′-alkylazoxybenzene.

4,4′-dialkylazoxybenzenes.[24] This dependence is shown in Figure 2 for three compounds belonging to the homologous series I as a function of the temperature difference $t - t_c$. The values of all three refractive indeces decrease with growing length of the alkyl chain. This tendency is especially visible for the refractive index in the isotropic phase as shown in Figure 3 at temperature $t - t_c = +5°$. The n_i values show a small alternation depending on the number m of carbon atoms in C_mH_{2m+1}, Compounds with even m values have higher refractive indeces n_i in the isotropic phase, the values of n_i in both series I and II differing insignificantly. On the contrary, the difference between the two homologous series of compounds are large as regards birefringence $\Delta n = n_e - n_0$.

The compounds belonging to series II with methyl as permanent terminal

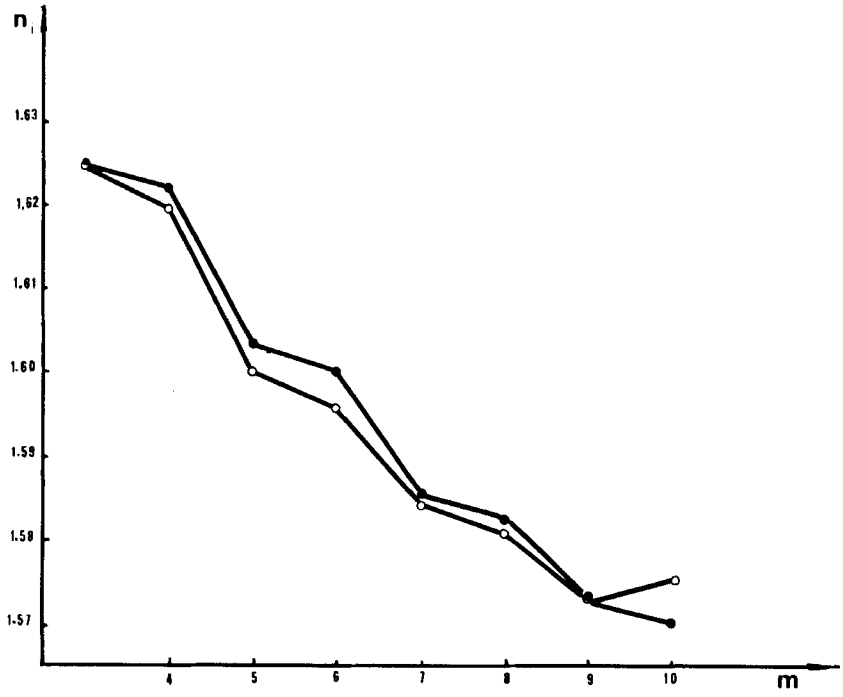


FIGURE 3 Refractive indexes in the isotropic phase as a function of the number of carbon atoms in the alkyl chain of 4-methyl-4′-alkylazoxybenzenes (full circles) and 4-ethyl-4′-alkylazoxybenzenes (empty circles).

substituent reveal much higher values of Δn than compounds belonging to series I with ethyl as permanent terminal substituent. The value of Δn depends in both homologous series on the length of the alkyl chain and is greatest for the heptyl radical. The values of anisotropy show systematically a strong alternation depending on whether the number of carbon atoms in the alkyl is even or odd (Figure 4). As distinguished from the isotropic phase the compounds with odd numbers of carbon atoms in the alkyl substituent have larger Δn values, which is consistent with the alternation of clearing points.

Dielectric constants The compounds belonging to both homologous series I and II reveal a small positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ assuming for $t - t_c = -5°$ values ranging from 0.6 to 0.1. The values of dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, ε_i and dielectric anisotropy $\Delta\varepsilon$ decrease with growing m (Figures 5, 6, 7 and 8). This feature also observed in other homologous series, as well as for 4,4′-dialkylazoxybenzenes[25] results from the decreasing density. The very significant alternation of dielectric

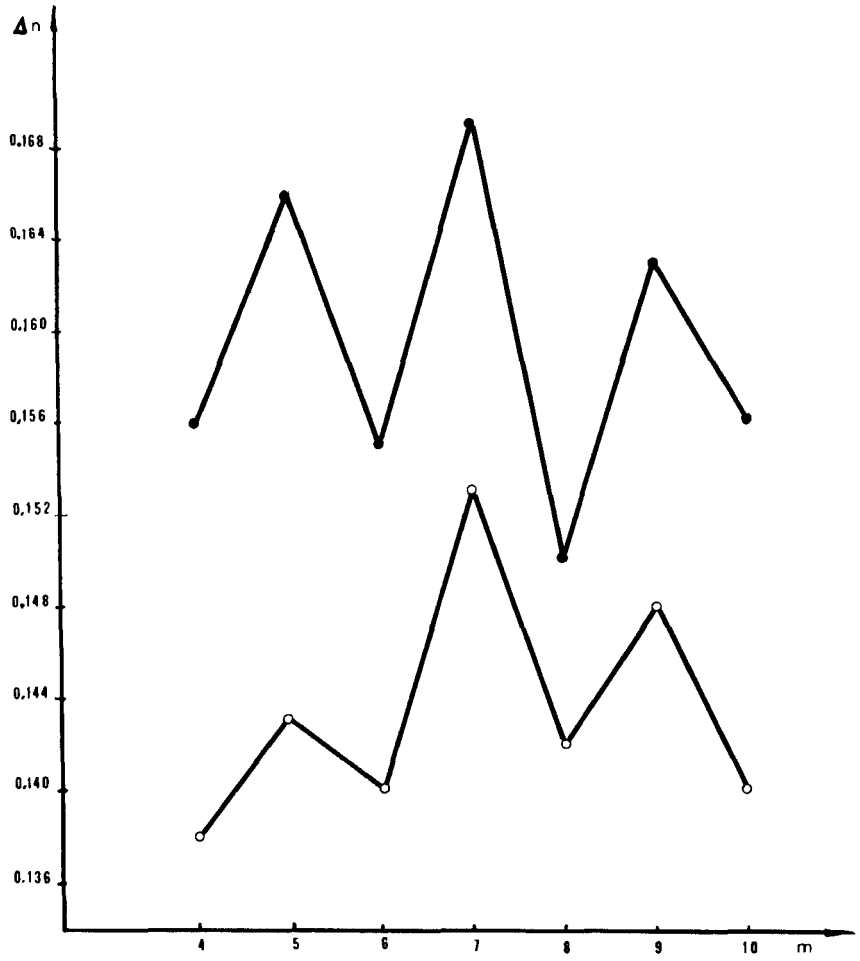


FIGURE 4 Birefringence Δn as a function of the number of carbon atoms in the alkyl chain for 4-methyl-4′-alkylazoxybenzenes (full circles) and 4-ethyl-4′-alkylazoxybenzenes (empty circles).

constant anisotropy $\Delta\varepsilon$ deserves special attention. The values of $\Delta\varepsilon$ are greater in both series of compounds for compounds with odd numbers of carbon atoms in the alkyl. The values of $\Delta\varepsilon$ are similar in both series of compounds when the values of m are the same (Figure 7).

In series I of compounds we observe for $m = 8$ (Figure 5) a nematic-smectic transition which is accompanied by a decrease of the $\varepsilon_{\parallel}$ value. Several degrees below the phase transition $N \rightarrow S_A$ temperature the dielectric anisotropy vanishes. In series II the variations of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ with temperature

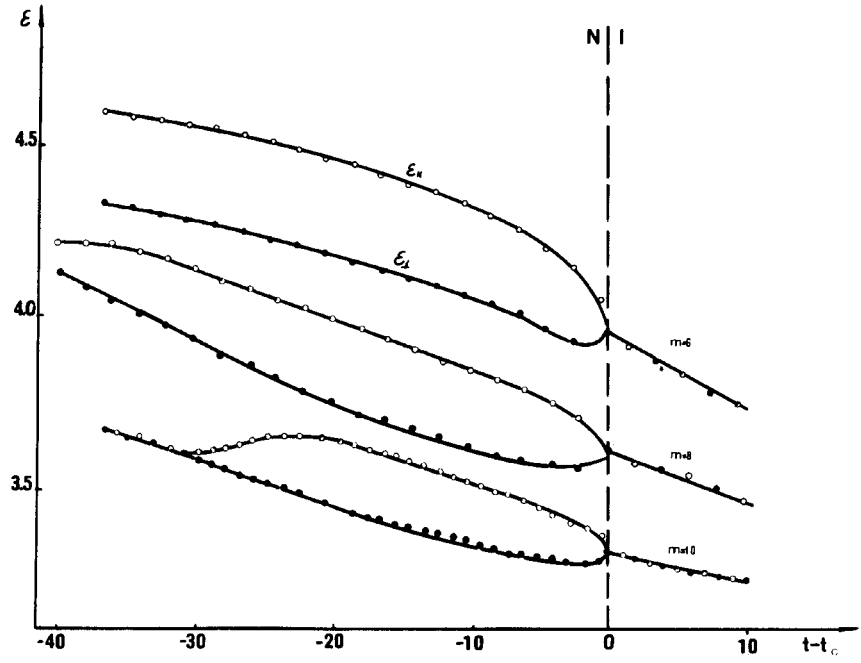


FIGURE 5 Variation of the dielectric constants: $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_i with temperature for compounds belonging to the 4-ethyl-4′-alkylazoxybenzene series.

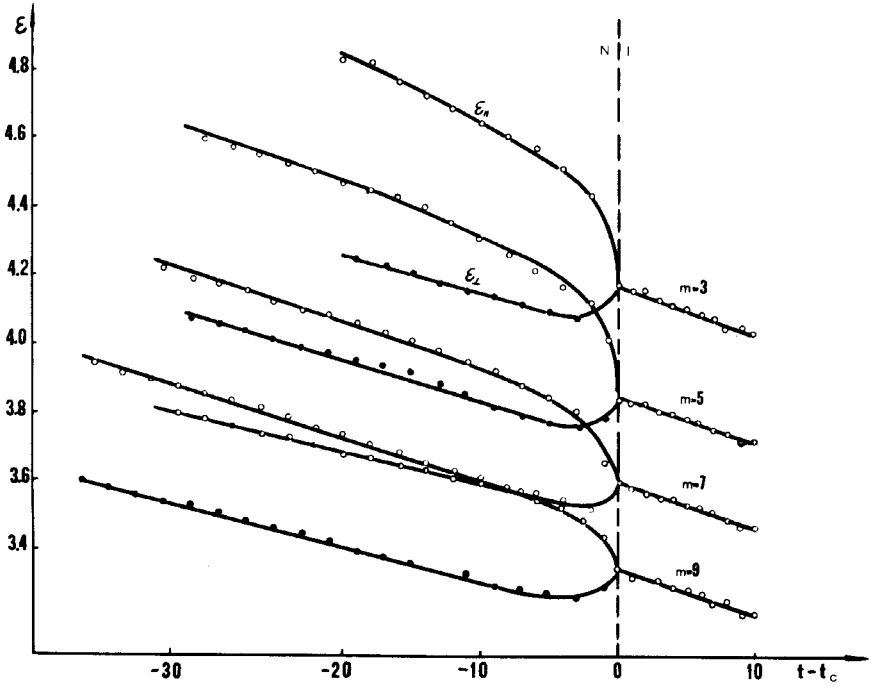


FIGURE 6 Variation of the dielectric constants: $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_i with temperature for compounds belonging to the 4-methyl-4′-alkylazoxybenzene series.

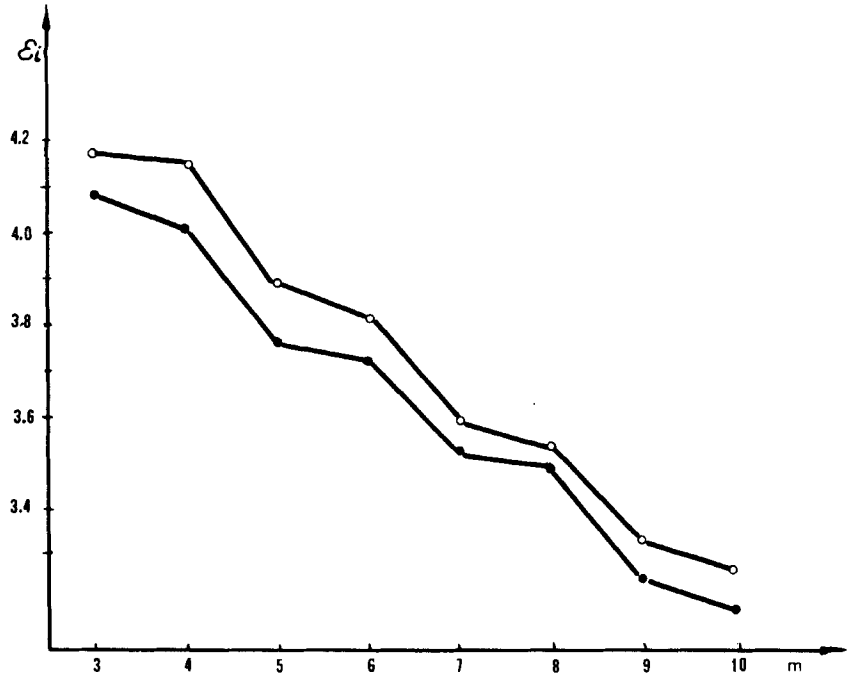


FIGURE 7 Dielectric constant in the isotropic phase as a function of the number of carbon atoms m in the alkyl chain: 4-ethyl-4′alkylazoxybenzenes (empty circles), 4-methyl-4′-alkyl-azoxybenzenes (full circles).

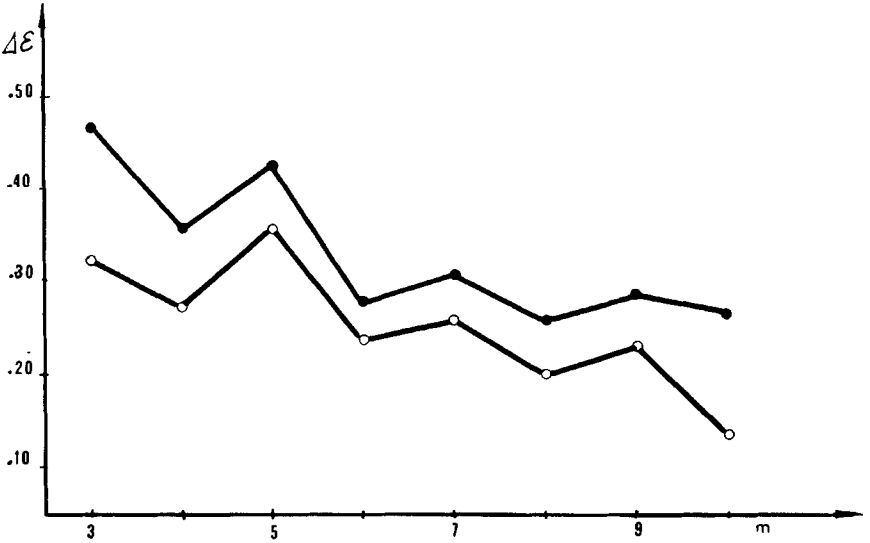


FIGURE 8 Dielectric anisotropy $\Delta\varepsilon$ as a function of the number of carbon atoms m in the alkyl chain: 4-ethyl-4′-alkylazoxybenzenes (empty circles) and 4-methyl-4′-alkylazobenzenes (full circles).

do not indicate that in those compounds a tendency occurs to build up a smectic ordering when the temperature is lowered (Figure 6) except the compound with decyl radical.

The Maier–Meier equation relates the dielectric anisotropy $\Delta\varepsilon$ and the ordering parameter S as follows:

$$\Delta\varepsilon = 4\pi NhF\left\{\Delta\alpha - F\frac{\mu^2}{2kT}(1 - 3\cos^2\gamma)\right\}S$$

where:

N is the number of molecules,
h is the cavity field factor,
F is the reaction field factor,
$\Delta\alpha$ is the anisotropy of induced polarizability,
μ is the permanent dipole moment,
γ is the angle between μ and the long molecular axis.

From this relationship it can be concluded that the observed $\Delta\varepsilon$ alternation results largely from the alternation of parameter S and $\Delta\alpha$ in dependence on the number of atoms m in the alkyl substituent. This problem will be given a detailed treatment in another work.[26]

Density The variations of the specific and molar volumes with temperature are given for three compounds from series I (for $m = 5, 8$ and 10) in Figure 9. The density of these compounds increases with decreasing length of the alkyl substituent. In the nematic and isotropic liquid ranges the density is a linear function of temperature and varies according to the formula:

$$d_t = d_0 + \alpha t$$

The values of the constants d_0, α and the standard deviation $\delta = \sqrt{\Delta^2/n - 1}$ as calculated by the least squares method from experimental data are listed in Table III. These data allow us to calculate the density at any temperature. In the case of the nematic-isotropic liquid transition as well as in that of the smectic-nematic transition (for $n = 10$) the transition effects are distinctly visible. Several degrees above and below the phase transition temperature the density variation deviates from linearity.

In the vicinity of the nematic-isotropic liquid phase transition we can calculate the density from the equation:

$$d'_t = d_t + A\left(\frac{|t_c - t|}{t_c}\right)^{\varepsilon}$$

The constants A and ε as well as the clearing temperature t_c found in pycnometric measurements are listed in Table III. The change of the molar volume

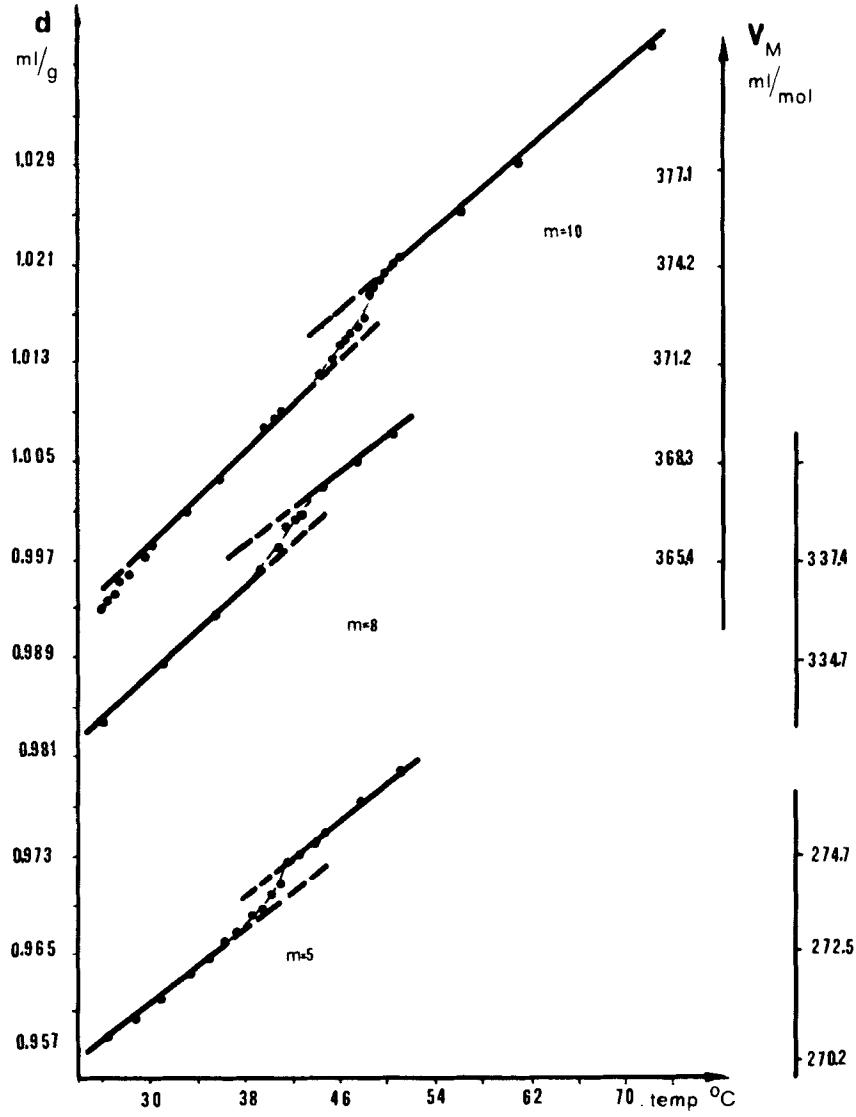


FIGURE 9 Variation of density with temperature for compounds belonging to the 4-ethyl-4′-alkylazoxybenzene series.

TABLE III

Value of constants for calculation density at various temperatures in 4-ethyl-4'-decyl- (a) and 4-ethyl-4'-pentylazoxybenzene (b)

Compound	Temperature range (°C)	d_o (g/ml)	$\alpha \cdot 10^4$ (g/ml, °C)	t_p (°C)	$A \cdot 10^4$	ε	σ
a	29.6 – 44.2	1.0346	−9.821				0.01
	44.2 – 48.0			48.09	1.346	−0.334	1.24
	48.2 – 50.1			48.09	54.64	0.616	2.26
	50.1	1.01837	−7.687				0.01
b	35.1	1.06578	−8.348				0.01
	35.1 – 40.7			47.75	795.8	−0.492	0.58
	41.7	1.06130	−7.940				0.01

on transition from the smectic to nematic phase is half that observed on transition from the nematic to isotropic phase and amounts to 0.11 mole % and 0.23 mole %, respectively, for $m = 10$. For compounds with $m = 5$ and 8 the change of molar volume on transition from nematic to isotropic liquid is 0.2 mole % and 0.16 mole %, respectively.

References

1. H. Kelker, B. Scheurle, R. Hatz, and W. Bartsch, *Angew. Chem.*, **82**, 984 (1970).
2. R. Steinsträsser, *Z. Naturforsch*, **27b**, 774 (1972).
3. Pat BRD 2 407 818.
4. M. A. Osman, *Z. Naturforsch*, **31b**, 801 (1976).
5. Pat BRD 2 352 151.
6. Pat BRD 2 526 520.
7. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Raynes, Proceedings of 166 National A.C.S. Meeting on Ordered Fluids and Liquid Crystals, Chicago, August, 1973, ed. R. S. Porter, J. F. Johnson, Plenum Press, N.Y., 1974, p. 617.
8. J. van der Veen and Th. C. J. M. Hegge, *Angew. Chem.*, **86**, 378 (1974).
9. K. Murase and H. Watanabe, *Bull. Chem. Soc. Japan*, **46**, 3142 (1973).
10. W. R. Young, A. Aviram, and R. J. Cox, *Angew. Chem.*, **83**, 399 (1971).
11. J. van der Veen and W. H. de Jeu, *J. Phys. Chem.*, **77**, 2153 (1973).
12. R. Dabrowski and K. Kenig, *Biul. WAT*, **27**, No. 3, 137 (1978).
13. K. H. Schündehütle, *Aromatische Azoxyverbindungen*, *Houben-Weyl*, **X/3**, 743 (1965).
14. J. van der Veen, W. H. de Jeu, A. H. Grobben, and J. Boven, *Mol. Cryst. Liq. Cryst.*, **17**, 291 (1972).
15. W. H. de Jeu, Th. W., Lathouwers, and P. Bordewijk, *Phys. Rev. Lett.*, **32**, 40 (1974).
16. J. W. Baran, J. Kedzierski, Z. Raszewski, and J. Zmija, *Biul. WAT*, **25**, No. 10, 37 (1976).
17. Z. Raszewski, Ph. D. Thesis, WAT, Warszawa, 1978.
18. J. W. Baran, F. Borowski, J. Kedzierski, Z. Raszewski, J. Zmija, and K. Sadowska, *Bull. Acad. Sci. Pol.*, **26**, 117 (1978).
19. J. Kedzierski, Ph.D. Thesis, WAT, Warszawa, 1978.
20. D. Demus, H. Demus, and H. Zaschke, *Flüssige Kristalle in Tablen*, VEB Deutscher Verlag für Grunstoffindustrie, Leipzig, 1974.
21. W. H. de Jeu and J. van der Veen, *Philips tech. Rev.*, **37**, No. 516, 131 (1977).

22. N. Campbell, A. Henderson, and D. Taylor, *Mikrochim. Acta*, **38**, 376 (1951).
23. M. V. Kurik, *Sol. State Phys.* (*Russ*), **19**, 1849 (1977).
24. W. H. de Jeu and P. Bordewijk, *J. Chem. Phys.*, **68**, 109 (1978).
25. W. H. de Jeu and Th. W. Lathouwers, *Z. Naturforsch*, **29a**, 905 (1974).
26. J. Kedzierski, Z. Raszewski, J. W. Baran, and R. Dabrowski, in preparation to press.