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Low Melting Liquid Crystalline *p,p'*-di-*n*-Alkylazoxy- and Azobenzenes

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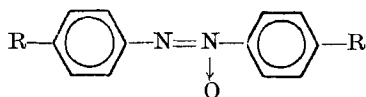
Abstract—The analogous series of *p,p'*-di-*n*-alkyl-substituted azoxy- and azobenzenes are synthesized. These compounds show low melting points and nematic or smectic behaviour. The melting points are generally lower for the azoxy compounds than for the analogous azo compounds. A probable explanation is the non-planar conformation of the azoxy compounds as compared with the planar conformation of the azo compounds. The influence of a permanent dipole moment in the azoxy series and the absence of a permanent dipole moment in the azo series is investigated. The clearing point is increased by the presence of a permanent dipole moment. The dielectric constants parallel and perpendicular to the molecular axis are measured for some typical members of the series. For both series we find $\epsilon_{\parallel} > \epsilon_{\perp}$, the difference being greater for the azo series than for the azoxy series.

1. Introduction

Recently a number of *p*-alkoxy, *p'*-*n*-alkyl substituted aromatic azo-⁽¹⁾ and azoxybenzenes,^(1,2) the latter mainly as a mixture of two isomers, have been synthesized which have much lower melting and transition points than the well known *p,p'*-di-*n*-alkoxy substituted azo- and azoxybenzenes. These results suggest that the permanent dipole moment has influence on the melting points as well as on the transition points. Therefore it seems worthwhile to compare the group moments of a methoxy group and a methyl group in a benzene nucleus. For a methoxy group the dipole moment is 1.28 D at an angle of 72° with the C_{ar}—O bond,⁽³⁾ for a methyl group the dipole moment is 0.37 D at an angle of 0° with the C_{ar}—C bond.⁽³⁾

Substitution of an alkoxy group by a *n*-alkyl group resulting in *p,p'*-di-*n*-alkyl substituted azo- and azoxybenzenes may lead to low melting liquid crystalline substances. Furthermore, it is important

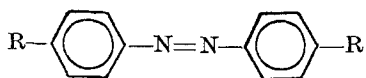
TABLE 1



R =	m.p. (°C)	S→N (°C)	N→I (°C)	No.
<i>n</i> -propyl	66–66.5		61.5 (mon.)	1
<i>n</i> -butyl	13.5–14.5		27.5	2
<i>n</i> -pentyl	22		65	3
<i>n</i> -hexyl	21.5–22		50.5	4
<i>n</i> -heptyl	34–34.5	53.5	71.5	5
<i>n</i> -octyl	40.5–41	67.5	69.5	6
<i>n</i> -nonyl	45–45.5		77.5†	7
<i>n</i> -decyl	50.5–51		77†	8

S = smectic, N = nematic, I = isotropic, mon. = monotropic, †S→I.

TABLE 2



R =	m.p. (°C)	N→I (°C)	No.
<i>n</i> -propyl	82–83	not mesomorphic	9
<i>n</i> -butyl	25–27.5	not mesomorphic	10
<i>n</i> -pentyl	48–49.5	37.5–38 (mon.)	11
<i>n</i> -hexyl	37.5–38	18–19 (mon.)	12
<i>n</i> -heptyl	39.5–40.5	46–46.5	13
<i>n</i> -octyl	48.5–49	40–40.5 (mon.)	14
<i>n</i> -nonyl	37.5–38	54–54.5†	15
<i>n</i> -decyl	43–44	53.5–54.5†	16

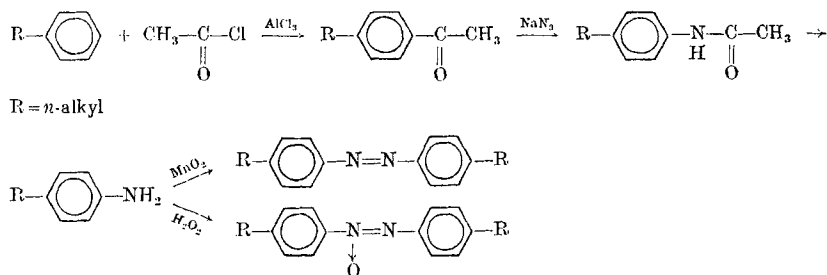
S = smectic, N = nematic, I = isotropic, mon. = monotropic, †S→I

to consider the influence of the p,p' -di- n -alkyl groups on the overall dipole moments of the corresponding azoxy and azo compounds. The group moments of two para n -alkyl substituents in azobenzenes in the stable *trans* configuration cancel each other, resulting in a zero dipole moment as that of azobenzene.⁽⁴⁾ For p,p' -di- n -alkyl substituted azoxybenzenes one can expect about the same dipole moment as in azoxybenzene although these compounds do not have an exact *trans* configuration.^(4,7)

The permanent dipole moment alone is inconclusive for forecasting liquid crystalline behaviour, since other properties, e.g. induced dipole moments and conformation, are important too. Analogous series of p,p' -di- n -alkylazoxybenzenes and azobenzenes are synthesized in which the overall dipole moments are non-zero and zero, respectively.

2. Results

The following reaction sequence was used for the synthesis of the azo- and azoxybenzenes. The starting products, n -alkylbenzenes, were commercial products.



The melting and transition points for the azoxy compounds are shown in Table 1, for the azo compounds in Table 2 (see also Figs. 1 and 2).

In both series an alternation of the clearing temperature (T_c) is found as a function of the number of carbon atoms in the R substituent (see Fig. 2). The melting and transition points were determined with a Reichert Thermopan polarizing microscope. The assumed structures were confirmed by N.M.R. and I.R. measurements

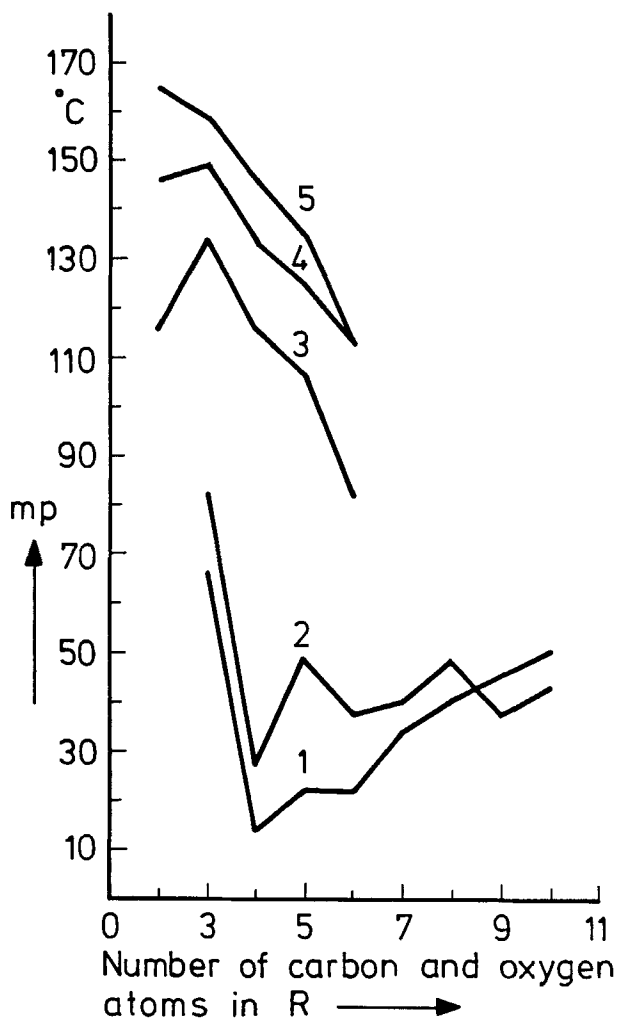
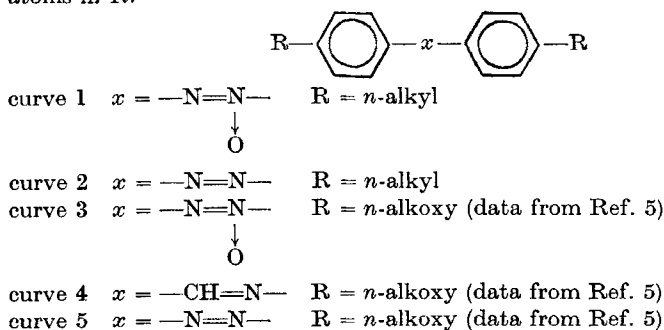


Figure 1. Melting points as a function of the number of carbon and oxygen atoms in R.



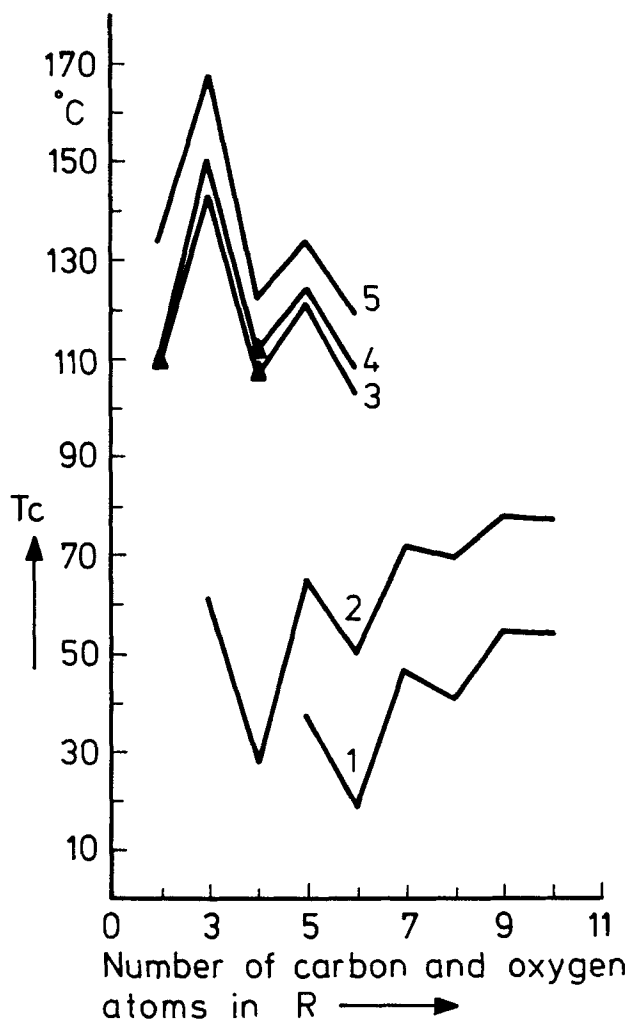
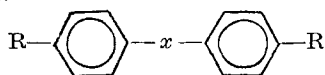


Figure 2. Clearing temperatures (T_c) as a function of the number of carbon and oxygen atoms in R.



curve 1 $x = \text{--N=N--}$ R = *n*-alkyl

curve 2 $x = \text{--N=N--}$ R = *n*-alkyl



curve 3 $x = \text{--CH=N--}$ R = *n*-alkoxy (data from Ref. 5 ▲ estimated figure)

curve 4 $x = \text{--N=N--}$ R = *n*-alkoxy (data from Ref. 5 ▲ estimated figure)

curve 5 $x = \text{--N=N--}$ R = *n*-alkoxy (data from Ref. 5)



TABLE 3 Elemental Analyses†

Compound No.	% C calc.	% C found	% H calc.	% H found	% N calc.	% N found
1	76.56	76.39	7.85	8.04	9.92	9.95
2	77.38	77.64	8.44	8.56	9.02	8.84
3	78.06	77.87	8.93	8.93	8.28	8.35
4	78.64	78.74	9.35	9.44	7.64	7.62
5	79.14	79.13	9.71	9.74	7.10	7.11
6	79.57	79.67	10.02	10.04	6.63	6.68
7	79.95	80.01	10.29	10.32	6.22	6.31
8	80.28	80.44	10.53	10.42	5.85	5.86
9	81.16	81.05	8.32	8.44	10.52	10.52
10	81.58	81.67	8.90	8.94	9.51	9.66
11	81.94	81.81	9.38	9.48	8.69	8.77
12	82.23	82.03	9.78	9.84	7.99	8.03
13	82.48	82.37	10.12	10.15	7.40	7.43
14	82.70	82.38	10.41	10.56	6.89	6.88
15	82.89	82.83	10.67	10.66	6.44	6.47
16	83.05	82.85	10.89	10.93	6.05	6.15

† Elemental analyses were carried out under the supervision of W. J. Buis at the Micro-Analytical Department of the Institute for Organic Chemistry T.N.O., Utrecht, The Netherlands.

TABLE 4 Dielectric Constants Parallel and Perpendicular to the Molecular Axis

Compound No.	ϵ_{\parallel}	ϵ_{\perp}
2	4.17	3.98
3	4.04	3.76
4	3.78	3.63
11	2.8	2.5
13	2.8	2.5

Nos. 2, 3 and 4 at 23°: Nos. 11 and 13 approximate values measured while the sample was cooled down.

as well as by the elemental analyses which are given in Table 3.† Table 4 indicates the static dielectric constants parallel and perpendicular to the molecular axis for some typical nematic compounds in the series. The constants were derived from capacity measurements on nematic species uniformly aligned by a magnetic field. The capacities were determined at a frequency of 1592 Hz with a Wayne and Kerr universal bridge B 221.

3. Discussion

Two *n*-alkyl groups as para substituents in azoxy- and azobenzenes result in compounds with low melting and transition points, as expected. In general (except for compounds 7 and 8) the azoxy compounds show lower melting points than the analogous azo compounds. The same behaviour is found for the symmetrically substituted *p,p'*-di-*n*-alkoxy azoxy and azo compounds⁽⁵⁾ (see Fig. 1). The results show also (see Fig. 2) that the azoxy compounds have systematically higher clearing temperatures (T_c) than the analogous azo compounds. Again the same behaviour is found for the symmetrically substituted *p,p'*-di-*n*-alkoxy azoxy and azo compounds⁽⁵⁾ (see Fig. 2).

Two factors are probably most important when considering the differences between the two *p-n*-alkyl substituted series. One is the presence of a permanent dipole moment in the azoxy compounds and the absence of a permanent dipole moment in the azo compounds. The other is the difference between the conformation of the planar azo compounds⁽⁶⁾ and the non-planar azoxy compounds.⁽⁷⁾ Dipole moments tend to increase the melting as well as the clearing point. Deviations from planarity tend to give the opposite effect.^(8,9) The lower melting points of the azoxy compounds compared with the analogous azo compounds could thus be explained by assuming that the difference in conformation is the dominant factor. The higher clearing points of the azoxy compounds compared with the

† Gaschromatographic analysis (at 225°C) of compound 2 showed the presence of 0.8% of compound 10. The gaschromatographic analyses of the other azoxycompounds had to take place at higher temperatures. At these temperatures however these compounds showed decomposition, making reliable analyses impossible. Gaschromatographic analyses of compounds 10 and 12 gave no indication of the presence of compound 2 and 4, respectively.

analogous azo compounds could be explained by assuming that the presence of a dipole moment is most important for this behaviour.

One should be careful in generalizing the explanations as given above. Compared with the azo compounds, the counter-acting effects of conformation and dipole moment lead for the azoxy compounds to lower melting and higher clearing points but for the also non-planar Schiff bases to both lower melting and clearing points (see Figs. 1 and 2).

The dielectric constant has a positive anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} > 0$) for all the nematic compounds measured. The contribution of the electronic polarizability to ϵ is greater parallel to the axis than perpendicular to it. Consequently for the azo compounds a positive $\Delta\epsilon$ can be expected because no permanent dipole moments are present. For the azoxy compounds there is an additional permanent dipole moment. In the first place this results in a higher average dielectric constant. As $\Delta\epsilon$ is not much changed compared with the azo compounds the dipole moment contributes clearly only slightly more perpendicular than parallel to the axis. Therefore the angle of the dipole moment with the axis of the molecule is probably slightly more than 55° .⁽¹⁰⁾ The compounds investigated do not show dynamic scattering in DC or AC electric fields.⁽¹¹⁾

4. Experimental

p-n-propylacetophenone. 60 g (0.5 mole) of *n*-propylbenzene were added to a stirred solution of 80 g (0.6 mole) of aluminium chloride in 350 ml of carbon tetrachloride and 42.6 ml (0.5 mole) of acetylchloride at $0-5^\circ$. After stirring for an additional hour, the reaction mixture was poured into a mixture of 250 ml of concentrated hydrochloric acid and 500 g of ice. The organic layer was extracted twice with 250 ml of 2 N hydrochloric acid, once with 250 ml of sodium hydrogen carbonate solution and finally with 250 ml of water, followed by drying over molecular sieve (Merck, 4 Å) for three hours. The solvent was removed and the residue was distilled in vacuo, b.p. $82-90^\circ$ (1.0 mm Hg). Yield 70.5 g (88%).

p-n-propylacetanilide. 7 g (0.11 mole) of sodium azide were added in small portions to a stirred solution of 16.2 g (0.1 mole) of *p-n*-

propylacetophenone in 146 ml of 70% sulfuric acid, at 15 to 20°. To inhibit foaming, 50 ml of dichloromethane was added. After stirring for an additional half hour, the reaction mixture was poured into a mixture of 200 ml of ice water and 100 ml of dichloromethane. The aqueous layer was extracted twice with 50 ml of dichloromethane and the combined organic layers were washed with 50 ml of sodium hydrogen carbonate solution and water, respectively. A portion (150 ml) of dichloromethane was removed by distillation and the residual solution was poured into 150 ml of petroleum ether (60–80). The resulting precipitate was filtered off and dried in vacuo, m.p. 98.5–99.5°. Yield 14 g (80%).

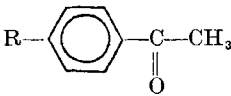
p-n-propylaniline. A mixture of 58 g (0.33 mole) of *p-n*-propylacetanilide, 275 g of sodium hydroxide, 550 ml of ethanol and 170 ml of water was refluxed for 5½ hours and distilled until the temperature of the residue reached 94°. The residue was poured into a mixture of 400 ml of water and 600 g of ice. The mixture was extracted twice with 250 ml of benzene. Thereupon the combined organic layers were extracted twice with 200 ml of water and dried with potassium carbonate. The benzene was distilled off and the residue was distilled in vacuo, b.p. 60–62° (0.5 mm Hg). Yield 38.4 g (85%).

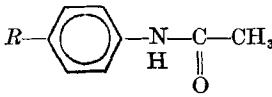
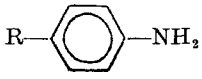
p,p'-di-n-propylazoxybenzene. (Similar to Ref. 12.) To a stirred solution of 20.5 g of acetonitrile, 200 ml of methanol, 12.4 g (0.09 mole) of *p-n*-propylaniline and a few drops of 2 N sodium hydroxide, 68 ml of 30% hydrogen peroxide was added at 35–40° and a pH of 9.5 (measured with a glass electrode and a calomel electrode as reference). The resulting solution was stirred for 5 hours at 35°. During the entire reaction a pH of 9.5 was maintained by addition of 2 N sodium hydroxide. The organic layer was separated and steam distilled. The resulting residue was crystallized twice from a mixture of ethanol and methanol (1 : 1) and once from a mixture of methanol and ethyl acetate (1 : 1), m.p. 66–66.5°. Yield 7 g (59%).

p,p'-di-n-propylazobenzene. (Similar to Ref. 13.) A mixture of 6.8 g (0.05 mole) of *p-n*-propylaniline, 250 ml of benzene and 26 g of manganese dioxide was refluxed for 6 hours. The water was removed azeotropically. The manganese dioxide was filtered off. The benzene

was distilled off and the residue was crystallized twice from methanol, m.p 82–83°. Yield 4.7 g (72%).

The intermediates had the following melting and boiling points and refractive indices. The *p*-*n*-butylaniline was obtained commercially (Aldrich Chem. Co., Inc.).

p - <i>n</i> -alkylacetophenones† 				
R =	b.p. (°C) (mm Hg)	m.p. (°C)†	n_D (°C)	
	found	literature	found	literature
<i>n</i> -propyl	82–90 (1)		1.5246 (20)	
<i>n</i> -pentyl	106–109(1.1)		1.5152 (20)	
<i>n</i> -hexyl	120 (1.1)	120 (1) ⁽¹⁴⁾	1.5126 (20)	1.5096 (25) ⁽¹⁴⁾
<i>n</i> -heptyl	129–135(1)		1.5106 (20)	
<i>n</i> -octyl	138–141(0.9)	149–150(1) ⁽¹⁴⁾	1.5070 (20)	1.5044 (25) ⁽¹⁴⁾
<i>n</i> -nonyl	148–150(0.9)	159–162(2–3) ⁽¹⁴⁾	1.5044 (20)	1.5039 (25.5) ⁽¹⁴⁾
<i>n</i> -decyl	36.5–37†	37–37.5† ⁽¹⁴⁾		

p - <i>n</i> -alkylacetanilides 		p - <i>n</i> -alkylanilines† 			
R =	m. p. (°C)	R =	b.p. (°C) (mm Hg)		
			found	literature	n_D^{20}
<i>n</i> -propyl	98.5–99	<i>n</i> -propyl	60–62(0.5)		1.5424
<i>n</i> -pentyl	100–102	<i>n</i> -pentyl	84 (0.55)	145–146(15) ⁽¹⁵⁾	1.5283
<i>n</i> -hexyl	90–92	<i>n</i> -hexyl	96 (0.6)		1.5233
<i>n</i> -heptyl	90–92	<i>n</i> -heptyl	106.5–107.5(0.6)		1.5206
<i>n</i> -octyl	93.5–94.5	<i>n</i> -octyl	118 (0.6)	138–140(5) ⁽¹⁵⁾	1.5159
<i>n</i> -nonyl	96.5–97.5	<i>n</i> -nonyl	126 (0.6)		1.5134
<i>n</i> -decyl	108–110	<i>n</i> -decyl	139 (0.6)		1.5106

† Gas chromatographic analyses indicated a purity higher than 97%.

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