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Mesomorphic Properties of Some Nitro Substituted Azomethines

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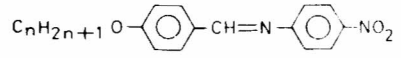
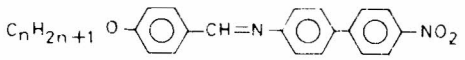
The homologous series of 4′-*n*-alkoxybenzylidene-4-nitroanilines (I) and 4″-*n*-alkoxybenzylidene-4′-amino-4-nitrobiphenyls (II) have been synthesized and their mesomorphic properties investigated. Generally, the alkoxybenzylidenenitroanilines show only monotropic nematic and smectic phases, whereas the biphenyl derivatives exhibit broad nematic and smectic phases. The smectic phases of the biphenyl compounds are of the S_B and S_E types which are scarcely observed for liquid crystals with polar terminal groups. X-ray studies show that the smectic phases of both the series exhibit bilayer structures.

Cyano substituted liquid crystals have been investigated in numerous studies because of their application in twisted nematic displays. The corresponding nitro derivatives have not achieved this technical interest because of their yellow colour and their low chemical and photochemical stability. In order to study the mesomorphic properties of these compounds in more detail, we have synthesized two homologous series of nitro compounds which are only partly known[1-5]: 4′-*n*-alkoxybenzylidene-4-nitroanilines (I) and the 4″-*n*-alkoxybenzylidene-4′-amino-4-nitrobiphenyls (II). Synthesis, mesomorphic properties and X-ray data are presented in this paper.



(I)



(II)

Materials and Methods

The azomethines were prepared by heating equimolar amounts of the alkoxybenzaldehydes and 4-nitroaniline or 4′-amino-4-nitrobiphenyl in toluene with a trace of *p*-toluenesulphonic acid. The reaction was performed *in vacuo* in order to remove water from the reaction. The products were purified by repeated recrystallization from appropriate solvents (hexane, ethanol). The compounds are very unstable to oxidation and hydrolysis and the clearing point temperatures decrease rapidly if the compounds come in contact with air.

Analytical data for 4″-*n*-octyloxybenzylidene-4′-amino-4-nitrobiphenyl (II, 8) are: MS (CI with 2-methylpropane): *m/z* 431(100), 401(15); ^{1}H NMR in $CDCl_3$ (ppm from TMS): 0.85(3H, triplet), 1.3(12H, multiplet), 4.0(2H, triplet), 6.9-8.4(13H, multiplet) (Found: C, 75.5; H, 7.0; N, 6.4. $C_{27}H_{30}O_3N_2$ requires C, 75.3; H, 7.0; N, 6.5%).

4,4′-Di-*n*-pentylbiphenyl was obtained from Merck and 4-nitrophenyl 4-*n*-octyloxybenzoate was synthesized in our laboratory.

The transition temperatures were determined using a polarizing microscope equipped with a heating stage. The mesophases were identified by their textures, X-ray studies and determination of binary diagrams of state which were obtained by means of the contact method.

Results and Discussion

Some of the compounds of series (I) have been synthesized in earlier investigations. However, the melting points of I, 3-I, 6, given in ref. 1, are more than 50K higher than the values from this work (Table 1)

Table 1—Transition Temperatures (in °C) for 4′-*n*-Alkoxybenzylidene-4-nitroanilines of Series I[a]

n	Cr	S_A	N	I
0	. 117	—	—	.
1	. 125	—	(. 85)	.
2	. 111	—	(. 71)	.
3	. 79	—	(. 62)	.
4	. 82	—	(. 72)	.
5	. 58	—	. 70	.
6	. 82	—	(. 80)	.
7	. 49	. 70	. 80	.
8	. 89	(. 83)	(. 85)	.
9	. 65	. 88	—	.

[a]Dots (.) indicate the existence of concerned modifications and dashes (—) the absence of transitions. Values in parentheses are temperatures for transitions to monotropic phases.

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and no mesophases were observed. For I, 5-I, 7 nematic phases with strongly deviating transition temperatures and no smectic phase for I, 7 were reported[3]. The low lying clearing point temperatures indicate that the compounds studied were partly decomposed.

Generally, series I shows only monotropic liquid crystalline phases (Fig. 1). I, 7 exhibits a fan-shaped texture in its smectic phase. The binary diagram of state (Fig. 2) with 4-nitrophenyl 4-*n*-octyloxybenzoate (NP8OB) shows that I, 7 exhibits a S_A phase. This is also true for I, 9 the smectic phase of which shows an uninterrupted miscibility with the S_A phase of I, 7 (Fig. 3).

The X-ray pattern of I, 7 shows at 55°C two sharp inner reflections lying parallel to the direction of the aligning magnetic field and two diffuse outer reflections in the perpendicular direction which is characteristic for a S_A phase. The *d*-value of 2.97 nm of the inner reflection corresponds to the spacing of the smectic layers and is 1.2 times the molecular length *l* of I, 7 determined with a Dreiding model. The observed bilayer formation is similar to the behaviour of cyano compounds[6] and other nitro compounds[7,8].

The short alkyl chain compounds of the biphenyl series II show only broad nematic phase ranges (Table 2, Fig. 4), whereas the higher homologues show additionally one or two smectic phases; the low temperature smectic phase is only monotropic. The binary diagram of state of II,5 and II,8 (Fig. 5) shows that the type of the smectic phases does not change within the series. The high temperature smectic phase exhibits a texture with lancets and homeotropic regions which is characteristic for S_B phases. The homeotropic regions become grey and concentric arcs appear at the transition to the low temperature smectic phase (S_E). The classification S_B and S_E is confirmed by the uninterrupted miscibility with the S_B and S_E phase of 4,4′-di-*n*-pentylbiphenyl[7] (55BP) shown in Fig. 6.

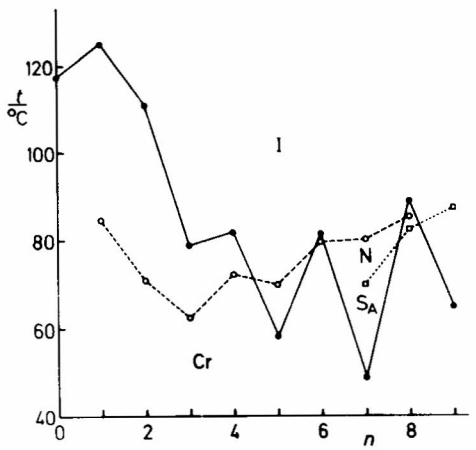

Fig. 1—Transition temperatures for the alkoxybenzylidenenitroanilines (I) as a function of the number (*n*) of the carbon atoms in the alkyl chain (●: melting point, ○: clearing point, □: S_A/N or S_A/I transition)

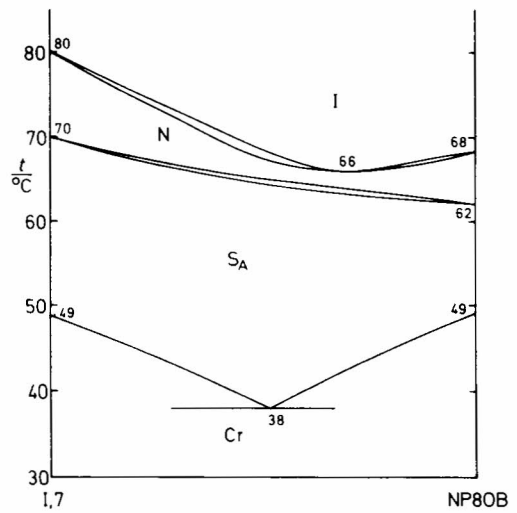

Fig. 2—Binary diagram of state of the system I, 7/4-nitrophenyl 4-*n*-octyloxybenzoate

Table 2—Transition Temperatures (in °C) for 4″-*n*-Alkoxybenzylidene-4′-amino-4-nitrobiphenyls of Series II[a]

n	Cr	S_E	S_B	N	I
0	178	—	—	194	
1	175	—	—	>350	
2	173	—	—	309	
3	146	—	—	291	
4	137	—	(125)	287	
5	111	(103)	141	272	
6	111	(99)	222	269	
7	98	(81)	237	256	
8	99	(93)	232	257	
9	93	(89)	254	—	

[a]See footnote in Table 1.

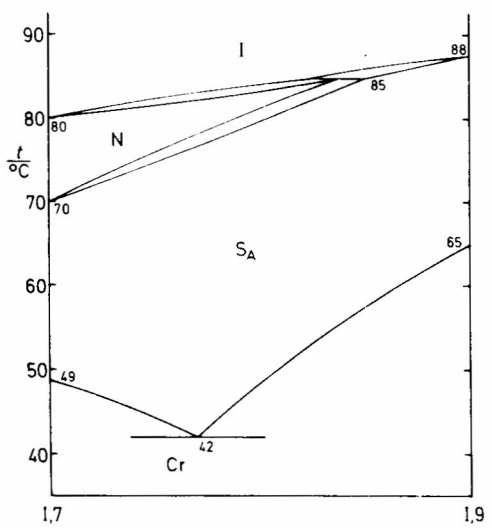

Fig. 3—Binary diagram of state of the system I,7/I,9

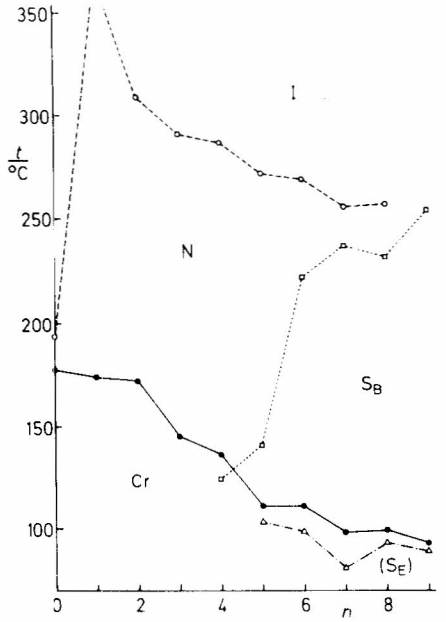

Fig. 4—Transition temperatures for the alkoxybenzylideneamino-nitrobiphenyls (II) as a function of the number (n) of the carbon atoms in the alkyl chain (●: melting point, ○: clearing point, □: S_B/N or S_B/I transition, Δ: S_E/S_B transition)

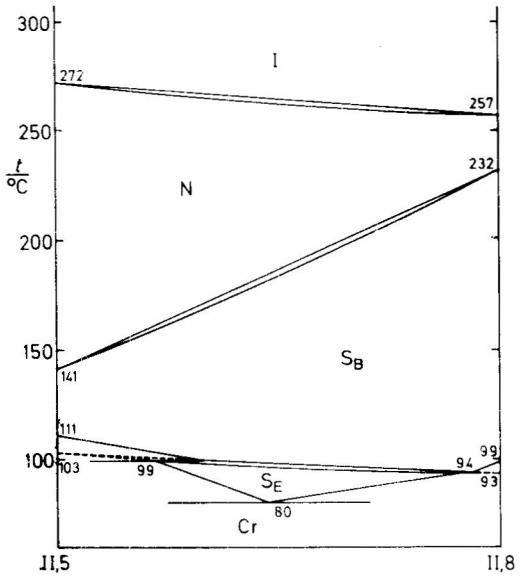

Fig. 5 – Binary diagram of state of the system II,5/II,8

The expected formation of a maximum in the transition temperature curves N/S_B or I/S_B due to the induction phenomenon of smectic phases[9] is not observed. Perhaps, the transition temperatures of the smectic phases of the compounds differ too much for the formation of a maximum and a non-linearity of the transition temperature curves can not be observed in a diagram of state which is deduced from measurements with the contact method.

The X-ray pattern of an unaligned sample of II,8 shows at 115°C (S_B phase) two sharp inner rings (d = 3.18 nm in 1. and 2. order) and one sharp outer ring (d = 0.435 nm). At 85°C (S_E phase) two sharp inner rings with the same d-value as in the S_B phase and three sharp outer rings (d = 0.443, 0.414, and 0.325 nm, respectively) are exhibited. The ratio d/l = 1.07 is smaller than the corresponding value in series I. Probably, this is caused by the larger overlap of the aromatic cores in series II as compared with series I.

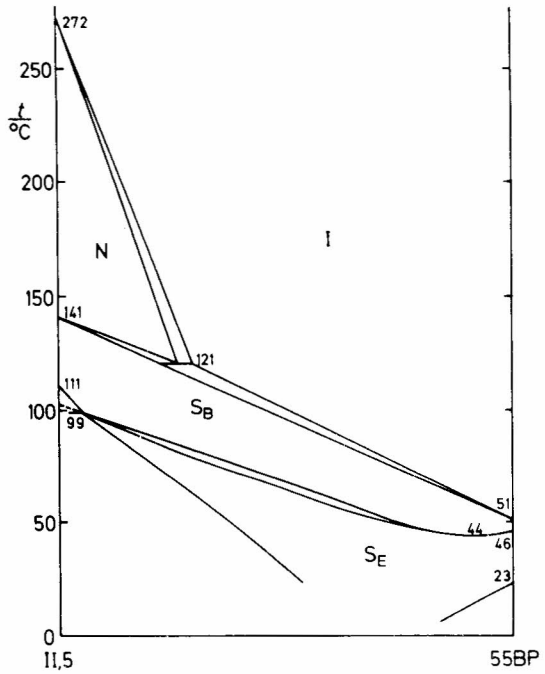

Fig. 6—Binary diagram of state of the system II,5/4,4'-di-*n*-pentylbiphenyl

A comparison of series I with the corresponding cyano derivatives[10] shows that the melting points are similar whereas the clearing points of the cyano derivatives are considerably higher. The formation of smectic phases is more pronounced for the nitro compounds than for the cyano compounds. Remarkable differences in the phase sequence of the smectic phases are found between the nitro and the cyano compounds[11] of the biphenyl series. Whereas both series exhibit S_B and S_E phases, the formation of S_A phases and reentrant nematic phases is only observed in the cyano series. In general, nitro compounds do not seem to exhibit reentrant nematic phases[12], although Pelzl *et al.*[13] report on this observation especially in mixtures.

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