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The Conformation of Aromatic Schiff Bases in Connection with Liquid Crystalline Properties†

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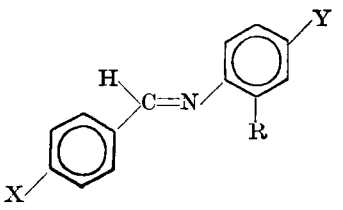
Abstract—Aromatic Schiff bases of the type



(R=H) exist in a stable non-planar conformation in which the angle between the plane of the N-phenyl group and the rest of the molecule is 40–60°, the so-called acoplanarity.[1] We suggest the molecule will become more rigid if an ortho substituent ($R=CH_3$) is introduced. A number of *p*-*n*-alkoxy, *p'*-*n*-acyloxy- and *p*-*n*-alkoxy, *p'*-*n*-alkoxy-N-benzylidene-anilines, with or without an ortho methyl substituent have been synthesized. These compounds show nematic liquid crystalline behavior. The introduction of an ortho methyl substituent, gives a depression both of the melting and the transition point. Compared with the unsubstituted analogue the thermodynamic stability of the nematic phase is also lowered. *p*-(*p*-methoxybenzylidene) amino-*m*-cresol acetic, butyric, hexanoic and decanoic acid ester are monotropic liquid crystalline at room temperature.

1. Introduction

Substantial quantitative evidence indicates that the assumption concerning Schiff bases being planar compounds analogous to azo compounds is invalid.

† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

(a) Evidence from UV spectra:

UV spectra of aromatic Schiff bases show a much lower intensity for the π–π^* transition of the —C(H)=N— electrons than that expected for a planar compound. Calculations based on UV spectra[1,2,3] show a twist angle of 55° for the aniline ring in N-benzylidene aniline, due to the steric hindrance of the two hydrogen atoms in the aniline ring upon the hydrogen atom of the azomethine group. Measurements of dipole moments indicate that aromatic Schiff bases have the trans configuration.[4]

(b) Evidence from X-ray analysis:

X-ray analysis shows that the aniline ring is twisted out of the C—N=C(H)—C plane by 55°, the benzylidene ring is twisted in the opposite direction by 10°.[5,11]

(c) Evidence from IR and NMR spectra:

Both NMR and IR spectra indicate that a para substituent in the aniline ring does not exert any appreciable effect on the azomethine group. This further suggests non-planarity in aromatic Schiff bases.[6]

Thus it is found that in a molecule such as N-benzylidene aniline, whether it is in solution or in the solid state, the minimum energy is reached in a non-planar conformation.

We assume that the same conformation exists in the liquid crystalline state.[10]

Introduction of an ortho substituent, such as a methyl group, produces two effects in concurrence with respect to the hydrogen substituted analogue. One effect, the formation of a larger twist angle, causes the molecule to become merely more rigid; thus the corresponding liquid crystalline properties remain present. Secondly, the molecule is broadened; thus there is a less favourable crystal lattice packing compared to that of the hydrogen substituted analogue, resulting in a lower melting point.

Samples of the above compounds were synthesized using their unsubstituted analogues to determine the validity of these assumptions.

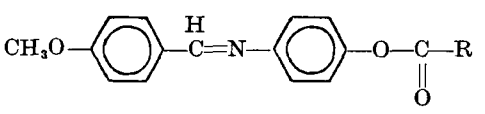
2. Results

A number of aromatic *p*-*n*-alkoxy, *p'*-*n*-acyloxy- and *p*-*n*-alkoxy, *p'*-*n*-alkoxy-N-benzylidene anilines, with or without an ortho methyl substituent have been synthesized. These compounds (with the exception of *20*) show nematic liquid crystalline phases. Compound *21* shows a nematic phase, just above its melting point, over a traject of 0.2°. The liquid crystalline properties were determined with a Reichert Thermopan polarizing microscope. No smectic phases could be detected, although some of the compounds are substituted with long alkyl chains. This could be due to the non-planar conformation of these compounds. In Tables 1, 2 and 3 the results for the different series are summarized. NMR and IR measurements as well as elemental analyses (Table 4) confirm the assumed structures.

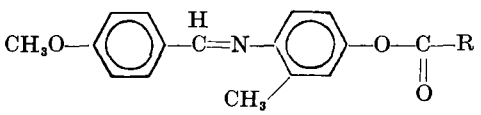
Enlarging the twist angle and broadening of the molecule does not lead to the disappearance of liquid crystalline behavior (except for 20), but is lowering the thermodynamic stability of the nematic phase.

The compounds *4*, *5*, *6* and *7* are monotropic liquid crystalline at room temperature. Except for compound *5* all ortho methyl-substituted compounds show lower melting and transition points than their unsubstituted analogues.

TABLE 1

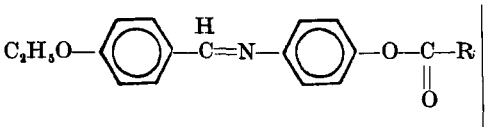


R	m.p. (°C)	nem.–isotrop. (°C)	No.
CH_3	81–82	108–109	Ref. 7
C_3H_7	54	115	1
C_5H_{11}	84–84.5	105.5	2
C_9H_{19}	75–75.5	92	3

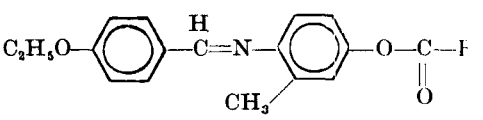


R	m.p. (°C)	nem.–isotrop. (°C)	No.
CH_3	74–75.5	26.5	4
C_3H_7	70–71	53	5
C_5H_{11}	47–48.5	46.5–47	6
C_9H_{19}	61.5–62	47.5	7

TABLE 2

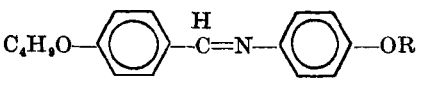


R	m.p. (°C)	nem.–isotrop. (°C)	No.
CH_3	112	134	8
C_3H_7	97.5–99.5	137	9
C_5H_{11}	78.5–79	110	10
C_9H_{19}	79.5	110–112	11

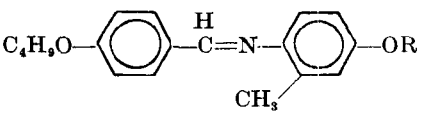


R	m.p. (°C)	nem.–isotrop. (°C)	No.
CH_3	89–89.5	65.5	12
C_3H_7	91–91.5	87	13
C_5H_{11}	68.5–70	71	14
C_9H_{19}	66.5–67	63	15

TABLE 3



R	m.p. (°C)	nem.–isotrop. (°C)	No.
C_6H_{13}	104.5–105	119	16
C_7H_{15}	98–100	116	17
C_8H_{17}	100–101	116.5	18
C_9H_{19}	101–102	113	19



R	m.p. (°C)	nem.–isotrop. (°C)	No.
C_6H_{13}	69.5–70.5	isotropic	20
C_7H_{15}	77–78	very small trajet	21
C_8H_{17}	50.5–51	68	22
C_9H_{19}	61–62	64	23

TABLE 4 Elemental Analyses

No.	%C calc.	%C found.	%H calc.	%H found.	%N calc.	%N found.
1	72.71	72.61	6.44	6.56	4.71	4.71
2	73.82	73.36	7.12	7.14	4.31	4.29
3	75.56	74.78	8.19	8.14	3.69	3.65
4	72.07	72.04	6.05	6.29	4.94	4.93
5	73.28	73.38	6.80	6.92	4.50	4.46
6	74.31	74.32	7.42	7.68	4.13	4.15
7	75.91	75.71	8.41	8.53	3.55	3.52
8	72.07	72.13	6.05	6.12	4.94	4.98
9	73.28	73.37	6.80	6.98	4.50	4.56
10	74.31	73.89	7.42	7.56	4.13	4.19
11	75.91	75.22	8.41	8.57	3.55	3.50
12	72.71	72.81	6.44	6.51	4.71	4.72
13	73.82	74.02	7.12	7.21	4.31	4.34
14	74.75	74.73	7.70	7.79	3.97	3.83
15	76.25	76.18	8.61	8.75	3.42	3.38
16	78.14	77.74	8.84	8.70	3.97	4.00
17	78.43	78.22	9.65	9.32	3.81	3.81
18	78.70	78.16	9.25	9.14	3.67	3.62
19	78.94	78.78	9.43	9.40	3.54	3.51
20	78.43	78.27	9.05	9.11	3.81	3.84
21	78.70	78.88	9.25	9.37	3.67	3.71
22	78.94	78.84	9.43	9.57	3.54	3.55
23	79.17	79.18	9.60	9.67	3.42	3.39

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

3. Experimental

Preparation of p-(p-methoxybenzylidene)amino-m-cresoldecanoic acid ester (7). Identical experimental procedures are used to prepare *1–15.*

p-(p-methoxybenzylidene)amino-m-cresol: A solution of 68 g (0.5 mole) of *p*-methoxybenzaldehyde, 61.5 g (0.5 mole) of 4-amino-*m*-cresol and a catalytic amount of *p*-toluenesulfonic acid in 500 ml of benzene is refluxed four hours while the water is removed azeotropicly. The solution is cooled and the resulting precipitate collected and dried *in vacuo.* Yield: 109 g (91%), m.p. 124–126°.

p-(p-methoxybenzylidene)amino-m-cresol decanoic acid ester: A solution of 24 g (0.1 mole) of *p*-(*p*-methoxybenzylidene)-amino-*m*-

cresol and 32.7 g (0.1 mole) of decanoic acid anhydride in 50 ml of pyridine is mixed thoroughly for three hours at 100 °C. The solution is then introduced into 400 ml of 1 N NaOH. The resulting precipitate is collected, dried over P_2O_5 and recrystallized twice from ethanol. The crystals are dried *in vacuo*. Yield: 22 g (58%) m.p. 61.5–62°.

Preparation of p-(p-butoxybenzylidene)amino-3-methyl-octyloxybenzene (*22*). Identical experimental procedures are used to prepare *16–23*.

p-butoxybenzaldehyde: A mixture of 61 g (0.5 mole) of *p*-hydroxybenzaldehyde, and 92 g (0.5 mole) of *n*-butyliodide is added to a solution of 40 g of KOH in 500 ml of 1-pentanol, refluxed five hours, and added to 350 ml of cold water. The 1-pentanol layer is separated and washed twice with 100 ml of water.

The aqueous washes are collected and extracted twice with 100 ml of ether. The ether extract is added to the 1-pentanol layer and the solvents are evaporated *in vacuo*.

The resulting residue is distilled *in vacuo*. Yield: 25 g (28%). b.p. 104–106° (2–3 mm Hg). (Ref. 8. 148–149° (10 mm Hg).)

p-(p-butoxybenzylidene)amino-m-cresol is synthetized from 25 g (0.14 mole) of *p*-butoxybenzaldehyde and 17 g (0.14 mole) of 4-amino-*m*-cresol as described for *p*-(*p*-methoxybenzylidene)-amino-*m*-cresol. Yield: 30 g (77%) m.p. 111–113°.

p-(p-butoxybenzylidene)amino-3-methyl-octyloxybenzene is synthetized from 7.1 g (0.025 mole) of *p*-(*p*-butoxybenzylidene)amino-*m*-cresol and 6.0 g (0.025 mole) of *n*-octyliodide as described for *p*-butoxybenzaldehyde. After removing the solvents, the residue is crystallized twice from methanol, and once each from petroleum ether (40–60°), and ethanol. Yield: 4.7 g (48%); m.p. 50.5–51°.

The other intermediates had the following melting points:

p-(*p*-ethoxybenzylidene)amino-*m*-cresol,	m.p. 147–149°.
p-(*p*-methoxybenzylidene)aminophenol,	m.p. 193.5–194° (Ref. 9 189°).
p-(*p*-ethoxybenzylidene)aminophenol,	m.p. 187.5–189.5°.
p-(*p*-butoxybenzylidene)aminophenol,	m.p. 145–147.5°.

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