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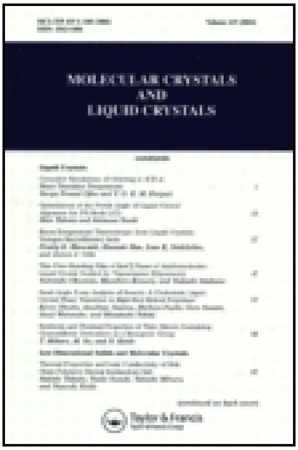

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The Effect on Thermal Nematic Stability of Schiff's Bases Upon Reversal of Terminal Substituents

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The Effect on Thermal Nematic Stability of Schiff's Bases Upon Reversal of Terminal Substituents

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Nematic liquid crystals have been found to produce dynamic light scattering when subjected to an electric field.⁽¹⁾ This electro-optic effect has stimulated widespread interest in the development of liquid crystals for display devices. It is desirable that the nematic material exhibit the nematic phase around ambient temperature and have a large mesomorphic range. No reported single component system meets these requirements although *bis*-(4′-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine has a reported 120° nematic range just above ambient temperature (59–179 °C).⁽²⁾

Kelker and Scheurle recently studied a series of anisilidene-*p*-alkyl anilines (Ia–e) in which they found the *n*-butyl (Id, Table 1) to have a nematic range of 20–41 °C.⁽³⁾ Replacement of the *n*-butyl substituent with *n*-propyl and *n*-amyl raised the transition temperature to 42–57 °C and 38–58 °C respectively, while ethyl and methyl substituents gave a monotropic phase.

It was of interest to us to study the effect of a systematic structural modification on the nematic properties of anils. In particular, this report is concerned with reversal of the terminal substituents in the above anils since lateral and terminal attractions are significant in determining nematic mesophase formation.⁽⁴⁾

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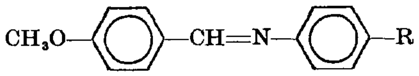
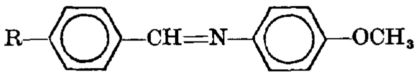
TABLE 1



I

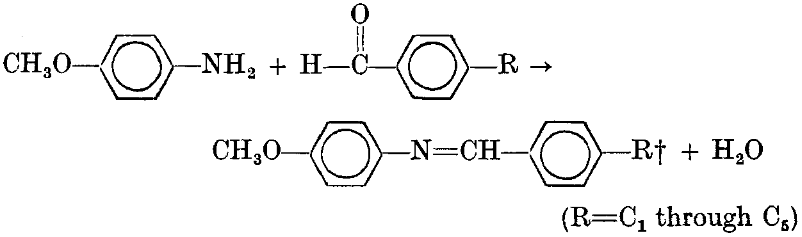


II

Compd.	R	M.P. (°C)	Transition Point Behavior (°C)†
Ia‡	CH_3	92–93	38 (monotropic)
IIa	CH_3	85.7–86.6	*i*
Ib‡	C_2H_5	57	28 (monotropic, n)
IIb	C_2H_5	60.5–61.5	*i*
Ic‡	n—C_3H_7	42	57 (enantiotropic, n)
IIc	n—C_3H_7	58–59	~57.5 (monotropic; H.N.) H.N. → n ~ 54; n → C ~ 28.5
Id‡	n—C_4H_9	20	41 (enant., n)
IId	n—C_4H_9	45.8–46.4	47.9 H.N. → *i*; 46.1 H.N. → n; < 43 n → C
Ie‡	n—C_5H_{11}	38	58 (enant., n)
IIe	n—C_5H_{11}	47.5	64.2 (H.N. → *i*) (enant., n)

† C = crystal; n = nematic; H.N. = homeotropic nematic; *i* = isotropic
‡ Ref. (3).

The series of reversed anils were prepared by the usual condensation of *p*-anisidine with the corresponding aldehyde:



The aldehydes, with the exception of *p*-methyl, were prepared by the method of Reiche, Gross and Hoeft.⁽⁵⁾ Table 1 compares the isomeric pairs of Schiff's bases.

With the exception of the methyl substituted compounds, members of series II had higher melting points than the isomers in series I. A similar trend is observed for the nematic-isotropic transition temperatures of the isomeric pairs with substituents larger than ethyl.

The inductive contributions of the heteroatoms to the dipole moment are opposing in series I and reinforcing in series II. The resonance interaction of the methoxy substituent opposes its inductive effect. The transition temperature trends apparently reflect a higher dipole moment for compounds in series II, implying that the inductive effects of the heteroatoms predominate.

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† GLC analysis indicated better than 99% purity and microanalyses were in satisfactory agreement with theoretical values.

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