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Mesomorphic Behaviours of Schiff's Base Compounds: I: N,N′-Di(4-n-Alkoxy-l-Naphthylidene)-Benzidines

J. S. Dave [a] , George Kurian [a] , A. P. Prajapati [a] & R. A. Vora [a]

[a] Chemistry Department, Faculty of Science M. S. University of Baroda, Baroda 2, India

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Mesomorphic Behaviour of Schiff's Base Compounds
I: N,N′-Di(4-*n*-Alkoxy-1-Naphthylidene)-Benzidines†

J. S. DAVE, GEORGE KURIAN, A. P. PRAJAPATI and R. A. VORA

Chemistry Department
Faculty of Science
M.S. University of Baroda
Baroda 2, India

Abstract—A homologous series of Schiff's base compounds has been synthesized to investigate the relationship between chemical constitution and mesomorphism, by condensing 4-*n*-alkoxy-1-naphthaldehydes with 4,4′-diaminodiphenyl (benzidine) and determining the transition temperatures of the compounds. It is observed that all the members of the series exhibit the general mesomorphic properties found in other analogous series. The first eight members of the series are nematic; the middle members are both smectic and nematic and the higher homologues, in analogy with the corresponding members of the similar series, are purely smectic. It is observed that the individual members of this series are comparatively less stable than the corresponding members of the N,N′-di(4-*n*-alkoxybenzylidene)-benzidine series. This can be attributed to the presence of the broad naphthalene nucleus in the present series.

Introduction

A number of homologous series$^{(1-6)}$ of organic compounds having a variety of molecular structures have been prepared and examined to investigate the relationship between chemical constitution and mesomorphism. It has been observed that when the alkyl chains are short, the systems are either non-mesomorphic or nematic, as the chain-length increases, smectic properties begin to appear, and as the smectic phase increases the nematic phase decreases with each successive chain increment, till in the higher homologues like hexadecyloxy and octadecyloxy derivatives, only smectic phases

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are found. It is also observed that when the transition temperatures are plotted against the number of carbon atoms in the alkyl chain, the transition points relating to the change mesomorphic to isotropic, generally fall on two curves, one relating to the derivatives with an odd number of carbon atoms in the alkyl chain, and the other to those with an even number.

Schiff's base compounds satisfy the minimum structural requirements for a compound to exhibit mesomorphism. *p*, *p*′-Disubstituted simple anils with two benzene rings and possessing terminal polar *n*-alkoxy groups and the mildly polar azomethine (CH : N) group at the centre are rectilinear polar molecules. These should be expected to show mesomorphism.

It seems that much less work is done in the synthesis of liquid crystalline substances containing broad naphthalene rings. The effect of the presence of naphthalene rings on mesomorphism should be quite interesting. With this object in mind in the present study, a homologous series of Schiff's base compounds was prepared by condensing 4-*n*-alkoxy-1-naphthaldehydes with benzidine and its mesomorphic behaviour studied.

Results and Discussion

A homologous series N,N′-di(4-*n*-alkoxy-1-naphthylidene)-benzidines is synthesized and the transition temperatures of the mesophases are summarized in Table 1.

The first eight compounds, starting from N,N′-di(4-methoxy-1 naphthylidene)-benzidine to N,N′-di(4-*n*-octyloxy-1-naphthylidene)-benzidine are all enantiotropic nematic. The smectic mesophase commences from the nonyloxy derivative as a monotropic smectic phase, whereas the decyloxy and the dodecyloxy derivatives exhibit enantiotropic smectic and nematic mesophases. The hexadecyloxy and octadecyloxy derivatives exhibit pure smectic mesophases in consonance with the other prototype homologous series, where the first few members having short alkyl chains, exhibit only the nematic mesophase, and the smectic mesophase appears in the middle members of the series due to the increment in the alkyl chain length; the last two members of the series exhibit only smectic mesophase.

Gray *et al.*(3), have studied the corresponding Schiff's base series

TABLE 1 N,N′-di(4-*n*-alkoxy-1-naphthylidene)-benzidines

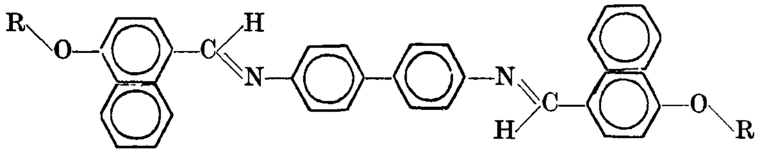
Alkyl group	Temperature of transitions, °C Smectic	Nematic	Isotropic
Methyl	—	297.0	313.0
Ethyl	—	268.0	318.5
Propyl	—	292.0	302.5
Butyl	—	244.5	300.5
Amyl	—	222.5	287.5
Hexyl	—	224.2	282.5
Heptyl	—	212.5	267.0
Octyl	—	203.5	260.5
Nonyl	(179.5)	180.5	246.2
Decyl	173.5	189.2	238.5
Dodecyl	162.5	199.0	221.7
Hexadecyl	144.0	—	196.0
Octadecyl	142.2	—	193.5

Value in parenthesis indicates monotropy.

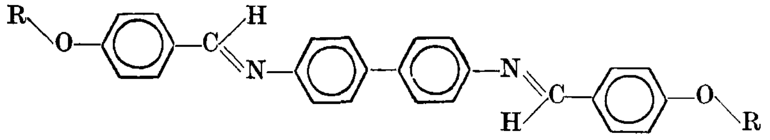
obtained by the condensation of *p*-*n*-alkoxybenzaldehydes with benzidine as well as with *p*-phenylenediamine. In these benzidine and *p*-phenylenediamine series of Gray *et al.*, the smectic phase appears respectively at the butyloxy and the amyloxy derivative, whereas in the present series the smectic phase commences with the nonyloxy derivative as a monotropic phase. The benzidine series in both cases are equal in length but the benzidine series in the present study contains naphthalene nuclei at the two ends of the molecules and is, therefore, comparatively broader than the corresponding *p*-*n*-alkoxybenzylidene-benzidine series. This will cause a considerable reduction in the lateral cohesive forces between the molecules in the present series and as such it is reasonable to expect that the smectic phase will appear at a later stage. In the alkoxybenzylidene-*p*-phenylenediamine series there are only three benzene rings and consequently the molecules will be comparatively shorter in length than in the present series. Here too the appearance of the smectic phase at a later stage in the present series than in the *p*-phenylenediamine series can be attributed to the greater breadth of the present series due to the broad naphthalene nucleus.

Dave and Patel⁽⁷⁾ studied the Schiff's base series obtained by the condensation of *p*-*n*-alkoxybenzaldehydes with *p*-*n*-amyloxy-, butoxyand propoxyanilines. In these three series the commencement of the smectic phase takes place respectively with the heptyloxy to nonyloxy derivatives. All these three series contain only two benzene rings with terminal polar groups and possess one middle azomethine group (CH : N) less than the other three series considered above. Naturally one may expect that the appearance of the smectic phase will be delayed, but it is interesting to note that this delayed appearance of the smectic phase coincides with the appearance of the smectic phase in the present series. This indicates that although the present naphthalene series possesses a greater length than the *p*-*n*-alkoxybenzylidene propoxyaniline series, the breadth of the present naphthalene series plays an important role in its mesomorphic behaviour.

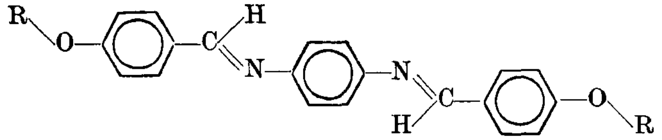
Dave and Patel⁽⁷⁾ also studied the *p*-*n*-alkoxybenzylidene-*p*-aminobenzoic acid series. In this series the smectic phase appears at the hexyloxy derivative stage. This series not only contains four benzene rings and two azomethine groups as in the present naphthalene series, but it is a little longer than the naphthalene series due to the presence of dimer carboxylic groups in the middle of the molecules and is less broad than the naphthalene series. Thus it is not surprising that the smectic phase in the aminobenzoic acid series should appear at a stage earlier than that in the present naphthalene series. The comparative geometry of the different series compared above is shown below:



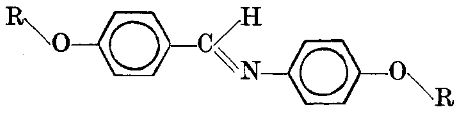
A

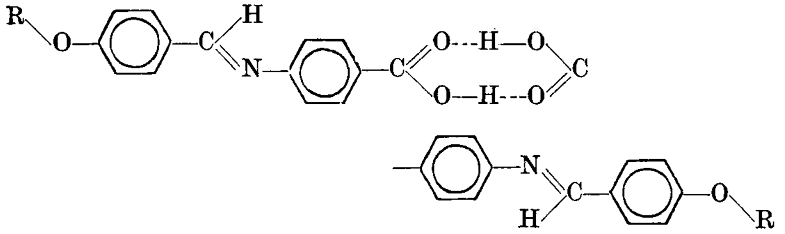


B



C


D


E

The following Table summarizes the corresponding comparative average thermal stabilities of the series, i.e. anils of 4-*n*-alkoxy-1-naphthaldehydes with benzidine(A), anils of *p*-*n*-alkoxybenzaldehydes with benzidine(B), with *p*-phenylene-diamine(C), with *p*-*n*-alkoxyanilines(D) and with *p*-aminobenzoic acid(E).

TABLE 2

Average transition temperatures (°C)	A	B	C	D	E
(i) Nematic-isotropic (C_5-C_{10}, C_{12})	257.7	351.5	238.9	110.0	249.0
(ii) Smectic-nematic or isotropic (C_9,C_{10},C_{12},C_{16},C_{18})	191.4	295.7	201.9	104.0	226.2

It can be seen from the above comparison of the average nematic and smectic thermal stabilities of the different series that the nematic thermal stability of the present series is higher than that of the series *C*, *D* and *E*. Series *D* contains only two benzene rings and also possesses one azomethine group less than the present series *A*; naturally the thermal stability of the series *D* should be less. The thermal stability of the nematic phase depends upon the ratio of the lateral cohesive forces to end-to-end cohesive forces; hence, the nematic phase will not depend solely upon the residual lateral cohesive forces, but also upon the terminal cohesive forces between the molecules. Therefore, an increase in the breadth is less effective in reducing the thermal stability of the nematic mesophase. Series *E* has almost the same length as the present series except that it has a dimer carboxyl group at the centre and a molecule of series *A* is broader than that of series *E*. If only length to breadth ratio is taken into consideration, then the nematic thermal stability of the series *A* should be less than that of series *E*, which is not the case. This can be explained by the high polarizability of the naphthalene nucleus and the conjugation in the molecule arising from the 1 : 1′ bond in diphenyl, which has enough double bond character to make a fully conjugated system possible in series *A*, resulting in the increase of end-to-end cohesions, compared to the acid dimer where the hydrogen bond will not transmit the effect of conjugation in the two dimer units and thus the polarizability of the molecules will be less in series *E* than in series *A*. In the case of series *C*, molecules are shorter in length than in series *A*. Naturally the thermal stability of the nematic mesophase for the series *C* should be less, because the breadth of the molecule in series *A* has comparatively less effect on the thermal stability of the nematic mesophase.

From this discussion it can be seen that in the present series the molecules are more polarized and broad than in the other series; so one can expect that the smectic mesophase in the present series should be thermally less stable. Reduction of the lateral cohesive forces and breadth of the molecule play an important role in the thermal stability of the smectic phase. Molecules try to maintain themselves against the disordering influence of thermal vibration, oriented parallel with their ends in line in the smectic mesophase. A close packing with the greater ratio of the lateral cohesive forces to end-to-end cohesive forces will, therefore, favour the formation of a thermally stable smectic mesophase. If the introduction of a suitable substituent increases the molecular breadth or thickness and there is no great increase in the dipole, the increased intermolecular separation will reduce the intermolecular forces and hence the thermal stability of the smectic phase will decrease. This is seen by the fact that the smectic thermal stability of the present series is less than that of *C* and *E*. The increase in the nematic thermal stability of series *A* over series *C* and *E* is 18.8 °C and 8.7 °C respectively, whereas the decrease in the smectic thermal stability of the present series *A* is 10.5 °C and 34.8 °C respectively, than that of series

C and *E*; the decrease in smectic thermal stability is thus suggestive of the pronounced effect of breadth on the smectic mesophase. Series *B* has the same length as series *A*, but the overall thermal stability of series *B* is much higher than that of the series *A*. Series *B* is effectively the same as series *A* except that the end benzene rings in series *A* have side substituents which bridge the 2- and 3-positions, resulting in the increase in the breadth of the molecules. This shows that the other factors remaining the same, the breadth of the molecule would play an important role in the overall stability of the mesophase.

It is interesting to note that although the thermal stability of the present series is smaller than that of series *B*, the decrease in the nematic thermal stability is 93.8 °C whereas the decrease in the smectic thermal stability is more, i.e. 104.3 °C, showing that breadth has a comparatively less pronounced effect on the nematic mesophase than the smectic mesophase. From the above results, it can be seen that not only the geometry of the molecules, but also length, breadth and polarizability of the molecules play an important role in the mesomorphic behaviour of potentially mesomorphic compounds.

Experimental

Determination of transition temperatures:

Preliminary measurements were made by the optical method of Dave and Dewar.(8) The precise measurements were, however, made with the polarizing microscope. To prepare the sample, the specimen was melted on a glass slide and a coverslip was pressed down on the liquid to get a thin section of the material. The slide was then inserted in the slide slot of the hot-stage fitted to a Leitz Ortholux Polarizing Microscope. In this electrically heated block, the sample could be observed continuously under carefully controlled temperature. The temperature in the neighbourhood of each change was raised at the rate of two degree/minute and the temperatures for various transitions were recorded by standard thermometers. The transitions were also checked by lowering the temperature slowly and observing the phase changes.

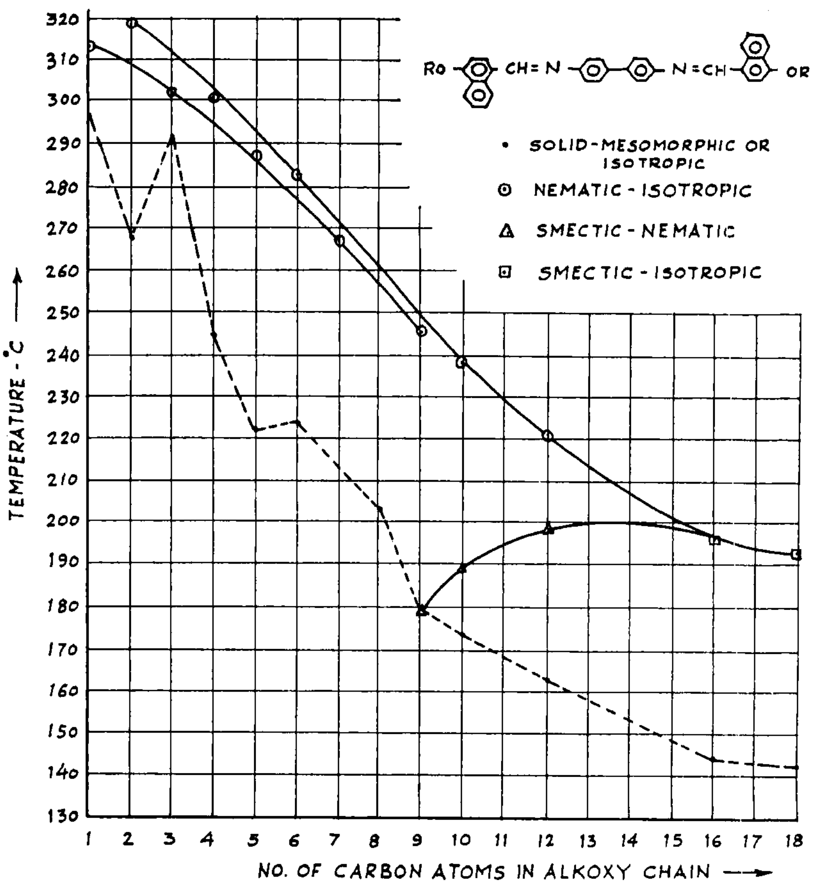


Figure 1.

(1) 4-*Hydroxy*-1-*naphthaldehyde:*

This was prepared according to the Gattermann synthesis.[9]

(2) *Synthesis of* 4-*n*-*alkoxy*-1-*naphthaldehydes:*[2]

4-Hydroxy-1-naphthaldehyde (1.0 mole), alkyl halide (1.5 mole) and anhydrous potassium carbonate (4.0 mole) were mixed in dry acetone and the reaction mixture was refluxed for about 8 hours on a water-bath. The solvent was decanted off. The bulk was then dissolved in water and the substance was extracted with ether. The ether was evaporated and the crude product was crystallized from ethyl alcohol. The melting points and the analyses of the substituted aldehydes are given in Table 3.

(3) *Schiff's bases:*

The Schiff's base compounds were prepared by refluxing 4-*n*-alkoxy-1-naphthaldehyde (2.0 mole) and 4,4'-diaminodiphenyl (benzidine) (1.0 mole) in ethyl alcohol for about 15 to 20 minutes and recrystallizing the product several times from appropriate solvents into fine crystals which give sharp melting points and transition temperatures. The analytical data are summarized in Table 4.

TABLE 3 4-*n*-Alkoxy-1-naphthaldehydes

Alkyl group	M.P. or B.P. (°C)	Form	Molecular formula	% Required		% Found	
				C	H	C	H
Methyl	210°/ 40 mm*	Pale yellow liquid	$C_{12}H_{10}O_2$	77.43	5.37	77.31	5.29
Ethyl	74.0**	Yellow needles	$C_{13}H_{12}O_2$	78.00	5.60	77.82	5.78
Propyl	69.2	Yellow needles	$C_{14}H_{14}O_2$	78.50	6.54	78.50	6.46
Butyl	59.5	Yellow needles	$C_{15}H_{16}O_2$	78.94	7.01	78.72	6.67
Amyl	68.0	Pale yellow needles	$C_{16}H_{18}O_2$	79.33	7.43	79.68	7.10
Hexyl	84.5	Pale yellow needles	$C_{17}H_{20}O_2$	79.68	7.81	79.60	7.81
Heptyl	66.7	Pale yellow needles	$C_{18}H_{22}O_2$	80.00	8.14	80.07	7.82
Octyl	73.5	Pale yellow needles	$C_{19}H_{24}O_2$	80.28	8.45	80.42	8.50
Nonyl	59.5	Pale yellow needles	$C_{20}H_{26}O_2$	80.54	8.72	80.76	8.49
Decyl	65.2	Pinkish needles	$C_{21}H_{28}O_2$	80.76	8.97	80.30	8.78
Dodecyl	70.5	Pinkish needles	$C_{23}H_{32}O_2$	81.17	9.41	80.89	9.39
Hexadecyl	77.7	Pale brown needles	$C_{27}H_{40}O_2$	81.81	10.10	81.36	9.70
Octadecyl	82.7	Pale brown needles	$C_{29}H_{44}O_2$	82.08	10.38	82.45	10.01

Reported * 212°/40 mm[10], ** 75.0 °C[10].

TABLE 4 N,N′-Di(4-*n*-alkoxy-1-naphthylidene)-benzidines

Alkyl group	Found % N	Molecular formula	Required % N	Solvent	Form
Methyl	5.44	$C_{36}H_{28}N_2O_2$	5.38	Diphenyl ether	Yellow needles
Ethyl	5.34	$C_{38}H_{32}N_2O_2$	5.11	Nitro-benzene	Yellow needles
Propyl	5.23	$C_{40}H_{36}N_2O_2$	4.86	Nitro-benzene	Yellow needles
Butyl	4.75	$C_{42}H_{40}N_2O_2$	4.63	Nitro-benzene	Yellow needles
Amyl	4.20	$C_{44}H_{44}N_2O_2$	4.43	Nitro-benzene	Yellow plates
Hexyl	4.42	$C_{46}H_{48}N_2O_2$	4.24	Nitro-benzene	Yellow plates
Heptyl	3.92	$C_{48}H_{52}N_2O_2$	4.07	Benzene	Yellow plates
Octyl	3.91	$C_{50}H_{56}N_2O_2$	3.91	Benzene	Yellow plates
Nonyl	3.55	$C_{52}H_{60}N_2O_2$	3.76	Benzene	Yellow plates
Decyl	3.54	$C_{54}H_{64}N_2O_2$	3.62	Benzene	Yellow plates
Dodecyl	3.24	$C_{58}H_{72}N_2O_2$	3.38	Benzene	Yellow plates
Hexadecyl	2.77	$C_{66}H_{88}N_2O_2$	2.98	Benzene	Yellow plates
Octadecyl	2.72	$C_{70}H_{96}N_2O_2$	2.81	Benzene	Yellow plates

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REFERENCES

1. Weygand, C. and Gabler, R., *J. Prakt. Chem.* **151**, 215 (1938); *Chem. Ber.*, **71B**, 2399 (1938).

2. Gray, G. W. and Jones, B., *J. Chem. Soc.* 4179 (1953); 1467 (1954).
3. Gray, G. W., Hartley, J. B., Ibbotson, A. and Jones, B., *J. Chem. Soc.*, 4359 (1955).
4. Gray, G. W., Hartley, J. B. and Jones, B., *J. Chem. Soc.* 1412 (1955).
5. Brown, G. H. and Shaw, W. G., *J. Amer. Chem. Soc.* **81**, 2532 (1959).
6. Gray, G. W., *J. Chem. Soc.* 552 (1958).
7. Dave, J. S. and Patel, P. R., *Mol. Cryst.* **2**, 103–123 (1966).
8. Dave, J. S. and Dewar, M. J. S., *J. Chem. Soc.* 4616 (1954).
9. Adams, R. and Levine, I., *J. Amer. Chem. Soc.* **45**, 2373–77 (1923).
10. Gattermann, L., *Ann.* **357**, 313 (1907).