Liquid Crystals

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Liquid crystals with a terminal oxime group

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Two homologous series with the terminal oxime group are synthesized to evaluate the effect of the oxime group on mesogenic properties of the system. It is observed that oxime formation eliminates the smectic mesophases exhibited by parent homologous series. The nematic phase exhibited by mesogens has higher thermal stability because of intermolecular H-bonding.

1. Introduction

A survey of the literature indicates that mesogenic compounds having an oxime group have been neither studied nor synthesized extensively. Burmistrov *et al.* reported mesogenic oximes of alkoxyazobenzenes [1]. Earlier, it was believed that free phenolic or alcoholic groups are not conducive to mesomorphism. Gray [2] has explained this lack of mesomorphism by taking into consideration the intermolecular hydrogen bonding which raises the melting point above the mesophase–isotropic liquid transition temperatures and may encourage a non-linear structural arrangement that is incompatible with mesophase formation, however additional research showed that phenolic hydroxy compounds can give mesophases of high thermal stabilities [3–5]. Goldmacher and McCafferey [6] reported mesogenic homologous series where the molecules contain a terminal alcoholic group.

We report here the synthesis of two homologous series with a terminal oxime group in order to study the mesogenic behaviour of these compounds.

2. Experimental

(1) 4-*n*-Alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chlorides were synthesized by the known methods of Dave and Vora [7].
(2) (4-*n*-Alkoxybenzoyloxy)benzaldehydes (series A) and 4-(4-*n*-alkoxybenzoyloxy)acetophenones (series B) were synthesized by the known method of Dave and Kurian [8].
(3) Oximes of series A and B were synthesized by the reported method [9].
(4) The oximes were recrystallized from methanol and ethanol until constant transition temperatures were obtained.
(5) The melting points and transition temperatures were determined by using Laborlux Leitz 12 POL microscope provided with a heating stage.
(6) The synthesized mesogens were characterized by elemental analysis and IR spectroscopy. The oxime linkage was confirmed by IR spectroscopy.

The transition temperatures are recorded in table 1.

Table 1. Series I and II compounds: transition temperatures (°C).

$R = C_nH_{2n+1}$ $n =$	Nematic	Isotropic
Series I		
1	—	—
2	—	160·0
3	—	120·0
4	88·0	128·0
5	87·0	111·0
6	89·0	117·0
7	79·0	109·0
8	78·0	113·0
10	75·0	111·0
12	74·0	108·0
14	76·0	106·0
16	70·0	105·0
Series II		
1	(76·0)[a]	159·0
2	(105·0)	170·0
3	(130·0)	166·0
4	(153·0)	162·0
5	128·0	147·0
6	110·0	140·0
7	122·0	135·0
8	98·0	133·0
10	104·0	126·0
12	90·0	123·0
14	92·0	121·0
16	101·0	121·0

[a] Values in parantheses indicate monotropy.

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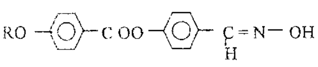
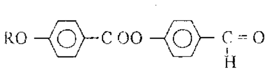
3. Results and discussion

The following two series of compounds were synthesized from the parent series A and B.

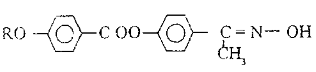
Series I



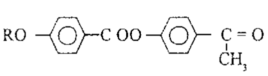
Series A



Series II



Series B



$R = n$-alkyl chain

The homologous series of oximes exhibit only the nematic phase; the smectic mesophase of the parent series is eliminated. The nematic mesophase is of higher thermal stability as compared with the parent series. The higher thermal stability of nematic mesophases may be attributed to the intermolecular hydrogen bonding. Table 2 summarizes the average nematic thermal stabilities of the present series as compared with the parent series.

Series II exhibits higher thermal stability than series I. This may be because of the molecular geometry of the two series. In series II, there is methyl group at the oxime end of the molecule while in series I, there is a hydrogen atom. Because of the presence of the larger methyl group, the molecules of series II will preferably be in the *anti* configuration while molecules of series I may have either a *syn* or *anti* configuration. It is known that, in general, *anti* isomers have higher melting points and absorb at longer wavelength λ, and more intensely than the *syn* isomers. The ultraviolet spectra of representative compounds of both the series corroborates this.

Series I, octadecyl derivative $\lambda_{\max} = 275{\cdot}2\,\mathrm{nm}$

Series II, hexadecyl derivative $\lambda_{\max} = 282{\cdot}0\,\mathrm{nm}$.

The plot of transition temperatures versus number of carbon atoms, n, in the alkoxy chain for series I (figure 1) shows the odd–even effect. The N–I transition temperatures show a falling tendency with increasing n.

For the series II compounds (figure 2), the first four members are monotropic nematic in nature and no odd–even effect is observed. The N–I curve first shows the rising tendency up to butoxy derivative and then levels off. This behaviour is discussed by Gray [2] for comparatively low melting series.

Table 2. Average nematic thermal stabilities of series I, II, A and B compounds (°C).

Homologues	Series I	Series A
n-butyl to n-octyl	113·0°C	68·0°C
	Series II	Series B
n-butyl to n-heptyl	143·0°C	88·0°C

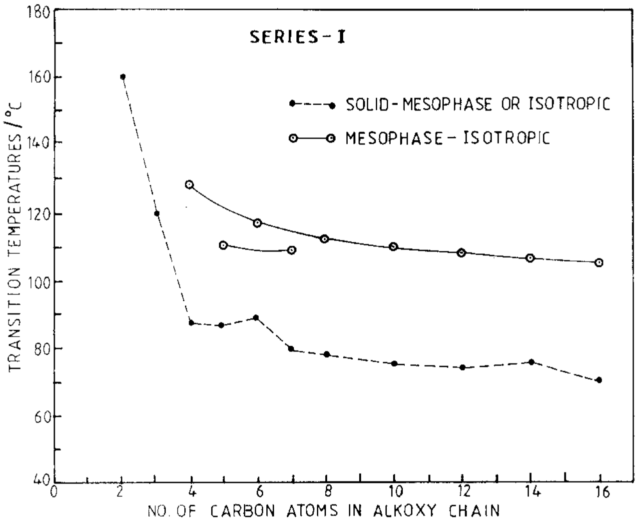


Figure 1. Series I compounds: transition temperatures versus number of C atoms.

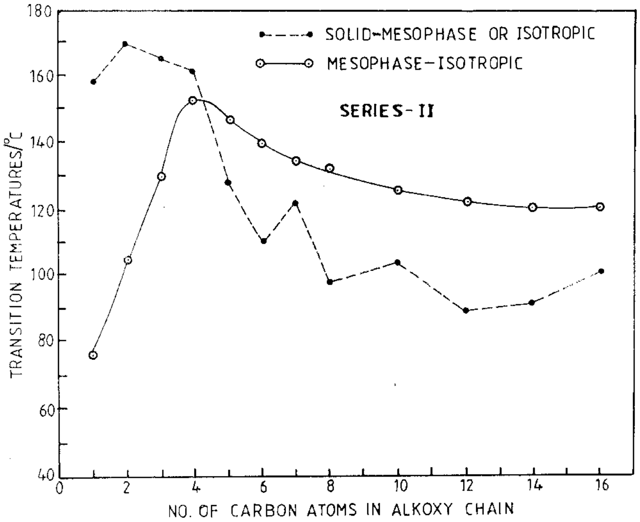


Figure 2. Series II compounds: transition temperatures versus number of C atoms.

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References

[1] Burmistrov, V. A., Kareev, V. Yu, Popova, T. V., and Koiyman, O. I., 1986, *Izv., Vyssh. Uchebn. Zaved. Khim., Khim. Technol.*, (Russ.), **29**, 122.

[2] Gray, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals*, (New York: Academic Press). 162.

[3] Vora, R. A., and Gupta, R. S., 1979, *Mol. Cryst. liq. Cryst. Lett.*, **56,** 31.

[4] Vora, R. A., and Gupta, R., 1980, *Liquid Crystals*, edited by S. Chandrasekhar (Heyden, Verlag), p. 589.

[5] Berdague, P., Bayle, J. P., Mei-Sing, Ho, and Fung, B. M., 1993, *Liq. Cryst.*, **14,** 667.

[6] Goldmacher, J. E., and McCafferey, M. T., 1970, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum Press), p. 375.

[7] Dave, J. S., and Vora, R. A., 1970, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (New York: Plenum Press). p. 477.

[8] Dave, J. S., and Kurian, G., 1975, *J. Phys. C*, **1,** 403.

[9] Vogel, A. I., 1994, *Text Book of Practical Organic Chemistry*, fifth edition, p. 1259.