

C H A P T E R



**Mesogenic triazene-1-oxides with
aldimine and ester units: synthesis,
characterization and thermal
properties**

CHAPTER V

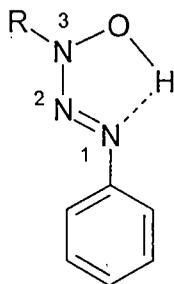
Mesogenic triazene-1-oxides with aldimine and ester units: synthesis, characterization and thermal properties

Abstract

The synthesis of a new group of triazene-1-oxides, $C_6H_5-N(O)=N-NH-C_6H_4-C(O)-O-C_6H_4-CH=N-C_6H_4-OR$, (**5**), [R = *n*-alkyl group; **5-1** (R = CH₃) to **5-14** (R = C₁₄H₂₉)], has been made. The compounds have been characterized by spectroscopic techniques. Elemental analysis data of all the compounds (**5-1** to **5-14**) confirm their proposed formulations. All the family members, consisting of four phenyl rings linked by one triazene-1-oxide, one ester and one aldimine groups with a terminal *n*-alkyloxy group, uniformly show thermotropic mesogenic behaviour. Here, the length of the alkoxy chain influences the mesogenic behaviour of the members. The compounds (**5-1** to **5-6**) (R = CH₃ to C₆H₁₃) of this new series show only nematic phase from melting temperature to the isotropic or clearing point. The compounds (**5-7** to **5-9**) (R = C₇H₁₅ to C₉H₁₉) exhibit smectic phase on melting followed by nematic phase up to the clearing point. Compounds (**5-10** to **5-14**) (R = C₁₀H₂₁ to C₁₄H₂₉) exhibit only smectic phase on melting.

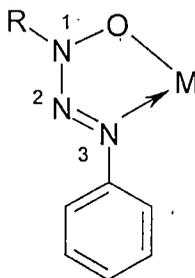
V. 1 Introduction

The synthesis of 3-hydroxytriazene (1) was first reported by Bamberger [1, 2]. The salt forming ability of the 3-hydroxytriazenes was also recognized by Bamberger [3], followed by Gebhard & Thompson [4].



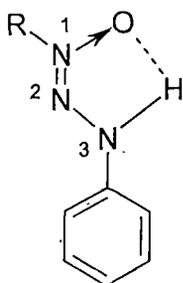
(1)

Elkins and Hunter examined [5] the chelating ability of 3-hydroxytriazenes and assumed that five membered chelate rings (2) were formed through the replacement of hydroxyl hydrogen and coordination of the azo nitrogen.



(2)

In 1965 Mitsuhashi et al. conclusively established that the actual structure of (1) is better described as the 3-aryl-1-alkyl(aryl)triazene-1-oxide (3). The triazene-1-oxide structural assignment was further supported by Chakravorty et al. using IR and PMR techniques. Saha et al. also confirmed the triazene-1-oxide structure by the X-ray structure [6].



(3)

The triazene-1-oxides and their substituted derivatives are known to have excellent metal binding properties. During last one hundred years, a large number of papers related to the metallo-derivatives of triazene-1-oxides have appeared in the literature. An excellent review article on the coordination compounds of triazene-1-oxides is available in the literature [7]. A brief summary of the important works done on the transition metal compounds of triazene-1-oxides since 1981 is given below.

Triazene-1-oxides and their substituted derivatives behave flexible ligand frame and offer a variety of stereochemistry with different metal ions. Triazene-1-oxide bis-chelates of Pd(II) reveal the *cis-trans* isomerism. The synthesis and structures of *cis*- and *trans*- geometrical isomers of bis(1-methyl-3-(*o*-tolyl)triazene-1-oxido)-palladium(II) was reported. Upon melting the *cis* isomer, it is spontaneously converted to the *trans* form [8]. The *cis-trans* isomerism and rotational isomerism in triazene-1-oxide bis-chelates of palladium(II) have been examined in details [9]. Terdentate triazene-1-oxides having thioether function binds nickel (II) in octahedral fashion and their magnetic and redox properties have been described [10]. Hexadentate behaviour of triazene-1-oxides incorporating thioether function is also known. The synthesis, structure and electron transfer properties of nickel(II) complexes [11] and a family of copper complexes were reported [12]

The electron transfer properties of groups of pseudooctahedral ML_3 and grossly planar CuL_2 complexes ($M = Fe, Co$; $L =$ triazene-1-oxide) have been reported [13].

The reversible dioxygen binding of high spin five coordinate Lewis base adduct of cobalt(II) triazene-1-oxide complexes has been studied [14, 15].

Catalytic behaviour of transition metal complexes of triazene-1-oxides is also known. The iron(III) and ruthenium(III) complexes of triazene-1-oxides are known to catalyze the epoxidation of alkenes with iodosylbenzene as an oxidant [16].

The triazene-1-oxides find extensive applications in analytical chemistry. Some of its applications in analytical chemistry have been described below.

The triazene-1-oxides have been widely used for spectrophotometric estimation of metal ions [17-37]. The estimation of fluorides, oxalates, phosphate, citrate, tartarate etc have been done using Fe(III) complexes of triazene-1-oxides using spectrophotometry following indirect method [26-28].

Suitably substituted derivatives of triazene-1-oxide have been reported as good metallochromic indicators for direct estimation of metal ions [38-39]. The iron(III) content of cement and different ores can be determined complexometrically with triazene-1-oxide as indicator. 3-*o*-Carboxysulphantophenyl-1-phenyltriazene-1-oxide can be used as an indicator in estimation of iron(III) with EDTA. The estimation can be done even in the presence of cobalt(II).

Gravimetric estimation of metal ions using triazene-1-oxide as precipitant is well known [17-19 & 40-47]. The gravimetric analysis of different metal ions using tridentate *o*-carboxylatophenyltriazene-1-oxides was described by Mazumdar et al [48]. Purohit dealt the gravimetric analysis involving monobasic bidentate triazene-1-oxides in his short review [49].

The 3-(*o*-nitrophenyl)-1-phenyltriazene-1-oxide is an useful reagent for the detection of zinc(II) and nickel(II) in presence of other metal ions. The 3-(*p*-nitrophenyl)-1-phenyltriazene-1-oxide can be used for the detection of magnesium(II). The above two reagents have been used for the colorimetric estimation of zinc(II) in ores and magnesium(II) contents in water or plant ash etc respectively.

The chemistry of 3-aryltriazene-1-oxides has biological relevance. The 3-aryltriazene-1-oxides and (pyridyl)triazene-1-oxide have been tested and their anti-inflammatory activities have been observed. [50]. Additional interest in triazene-1-oxides stems from their anti-tumour activity [51]. The 3-(4-carbamoylphenyl)-1-methyltriazene-1-oxide has activity against the TLX5 lymphoma and the AdjPC6/A plasmacytoma [52]. Interestingly its methoxy derivative 1-(4-carbamoylphenyl)-3-methoxy-3-methyltriazene does not show any activity. 1-(4-carbamoylphenyl)-3,3-dimethyltriazene-1-oxide has shown anti-tumour activity [53].

Mesogenic behaviour of triazene-1-oxides or their substituted derivatives is hitherto unknown. We have explored this area by designing and synthesis of new derivatives of triazene-1-oxides. The new group of compounds has been characterized by elemental analysis and spectroscopic techniques. The thermotropic mesogenic behaviour was detected by optical microscopy, DSC and small angle X-ray diffraction.

V. 2 Results and discussions

V. 2. 1 Synthesis

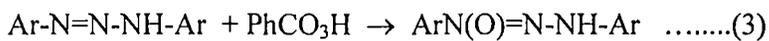
Bamberger and Busdorf first reported [1, 2] the synthesis of 3-hydroxytriazene, which was actually triazene-1-oxide, using the following route (1).



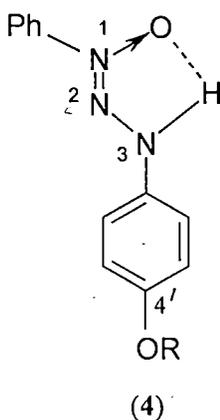
More convenient method was also developed by Bamberger [3]. The later method (2) involves the coupling of diazonium salts with alkyl or aryl hydroxylamine in 1:1 molar ratio.



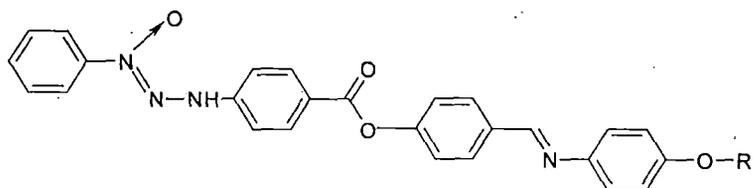
Mitsuhashi and Simamura [54] reported the formation of triazene-1-oxides by the oxidation of diazoaminobenzenes with peroxybenzoic acid:



The most widely used method for synthesis of triazene-1-oxide is route (2). We had made a series of 4'-*n*-alkyloxy-3-phenyl-1-phenyltriazene-1-oxides (4), which failed to show any thermotropic mesophases.

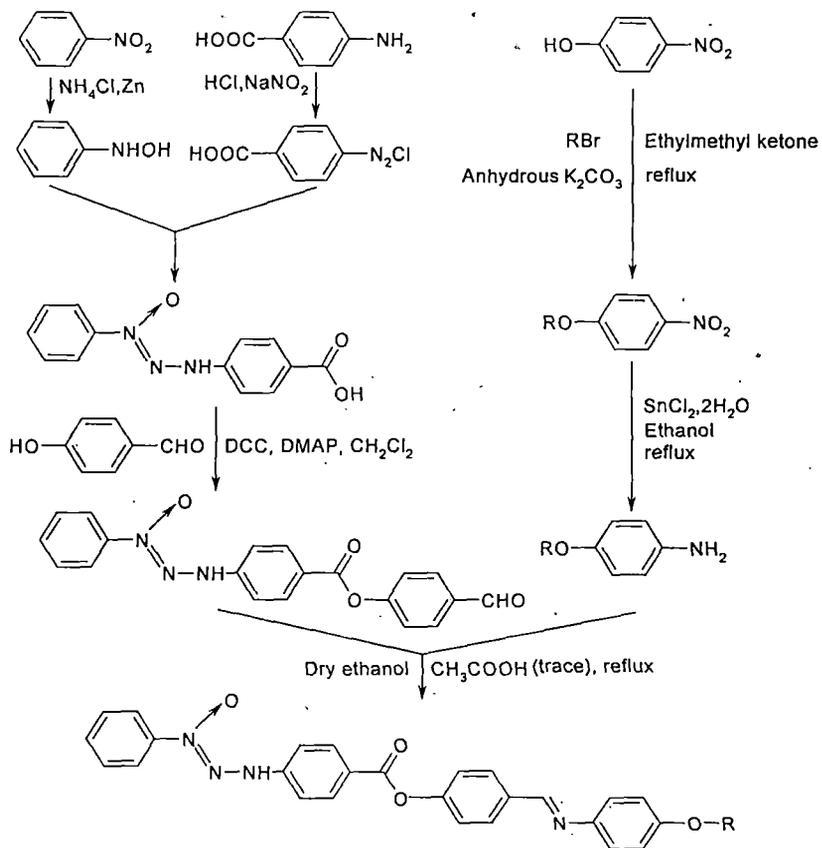


To introduce thermotropic mesogenic properties, we designed a derivative of (3; R=Ph), with two additional phenyl rings as rigid cores linked by ester and imine functions along with a flexible alkyloxy chain at one end as shown in (5).



(5)

The stepwise synthesis of (5) has been shown in Scheme V.1. The yield (%) for each member of this new homologous series has been given in Table V.1.



(5)

Scheme V. 1

Table V. 1 Yield (%) of the compounds (5-1 to 5-14).

Compound	R	Yield (%)	Compound	R	Yield (%)
5-1	CH ₃ -	42.3	5-8	C ₈ H ₁₇ -	66.4
5-2	C ₂ H ₅ -	40.8	5-9	C ₉ H ₁₉ -	68.5
5-3	C ₃ H ₇ -	53.7	5-10	C ₁₀ H ₂₁ -	73.4
5-4	C ₄ H ₉ -	56.4	5-11	C ₁₁ H ₂₃ -	82.3
5-5	C ₅ H ₁₁ -	70.8	5-12	C ₁₂ H ₂₅ -	65.5
5-6	C ₆ H ₁₃ -	72.5	5-13	C ₁₃ H ₂₇ -	71.3
5-7	C ₇ H ₁₅ -	62.9	5-14	C ₁₄ H ₂₉ -	67.8

V. 2. 2 Spectral properties

V. 2. 2. 1 Infrared spectra

The infrared spectral data of the compounds are collected in solid state as KBr disc and given in Table V.2. As a representative case the infrared spectrum of compound 5-12 is given in Fig.V.1. The IR spectra of all the compounds show absorptions in the range of 3212-3247 cm⁻¹ which are attributed to the N-H stretching vibrations. The lowering in stretching frequency compared to the normal $\nu_{\text{N-H}}$ stretching vibration establishes the presence of an intramolecular hydrogen bonding [55]. Strong absorptions in the regions of 1731-1740 cm⁻¹ and 1604-1612 cm⁻¹ for all the compounds show the presence of ester [56] and imine [57, 58, 59] groups respectively. The $\nu_{\text{-N=N-NH-}}$ (symmetric triazene) has been found as multiple band in the range of 1423-1504 cm⁻¹ [60]. The $\nu_{\text{N}\rightarrow\text{O}}$ stretch is observed as a medium band in the region of 1307-1319 cm⁻¹ [61]. The $\delta_{\text{N}\rightarrow\text{O}}$ (bending vibration) has been observed as split bands around 837 cm⁻¹ and 813 cm⁻¹.

Table V. 2 Infra-red spectral data^a for compounds (5-1 to 5-14).

Comp.	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=N}$		$\nu_{-N=N-N-}$		$\nu_{N \rightarrow O}$	$\delta_{N \rightarrow O}$	
5-1	3213m	1731s	1604s	1504s	1469s	1431m	1318m	837s	813w
5-2	3213m	1732s	1605s	1504s	1477s	1431m	1307m	837s	813w
5-3	3224m	1731s	1612s	1504s	1469s	1431m	1307m	848s	813w
5-4	3213m	1731s	1612s	1504s	1473s	1431m	1307m	837s	813w
5-5	3213m	1732s	1605s	1504s	1477s	1431m	1307m	833s	813w
5-6	3213m	1731s	1605s	1502s	1473s	1434m	1307m	837s	813w
5-7	3213m	1740s	1605s	1504s	1469s	1423m	1307m	837s	813w
5-8	3247m	1736s	1605s	1504s	1474s	1419m	1319m	837s	813w
5-9	3247m	1738s	1612s	1504s	1469s	1423m	1307m	848s	813w
5-10	3247m	1740s	1605s	1504s	1473s	1423m	1315m	837s	813w
5-11	3247m	1740s	1605s	1504s	1473s	1423m	1315m	837s	813w
5-12	3201m	1732s	1605s	1504s	1474s	1434m	1307m	837s	813w
5-13	3247m	1740s	1612s	1504s	1477s	1423m	1307m	837s	813w
5-14	3247m	1739s	1612s	1504s	1477s	1423m	1319m	844s	813w

^a KBr disc.

V. 2. 2. 2 Electronic spectra

The UV spectral data for the compounds 5-1 to 5-14 are summarized in Table V.3. The electronic spectra of all the compounds in dichloromethane were measured in the region 250-500 nm. The electronic spectrum of 5-13 has been shown in Figure V.2 as a representative case. The compounds (5-1 to 5-14) show two intense absorption bands at ~274 nm and ~356 nm. The absorption peak near 356 is supposed to be due to the presence of 'azo' group [62].

V. 2. 2. 3 ¹H NMR spectra

The ¹H NMR spectral data for 5-1 to 5-14 have been given in the Table V.4. A representative spectrum of 5-13 is shown in Fig. V.3. The low field signal ~10.9 δ corresponds to the intensity representing the N-H proton [63]. It is observed that the

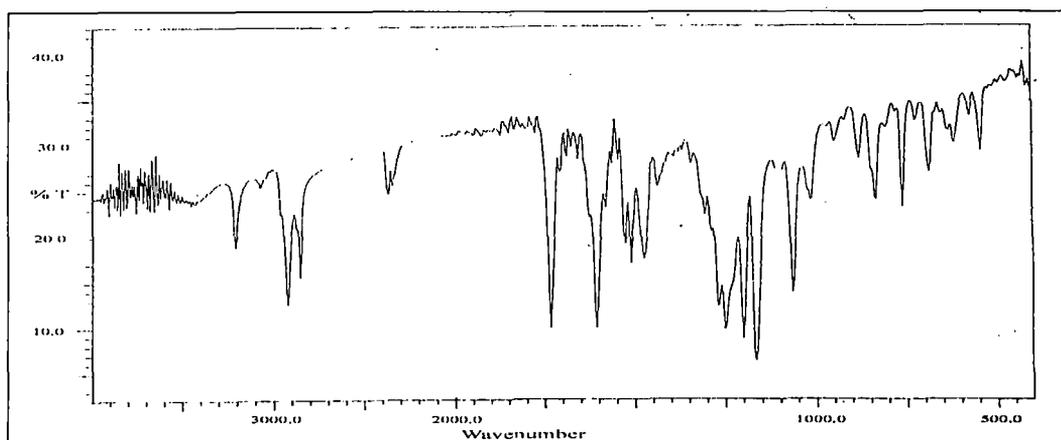


Figure V. 1 Infrared spectrum of 5-12 in KBr disc.

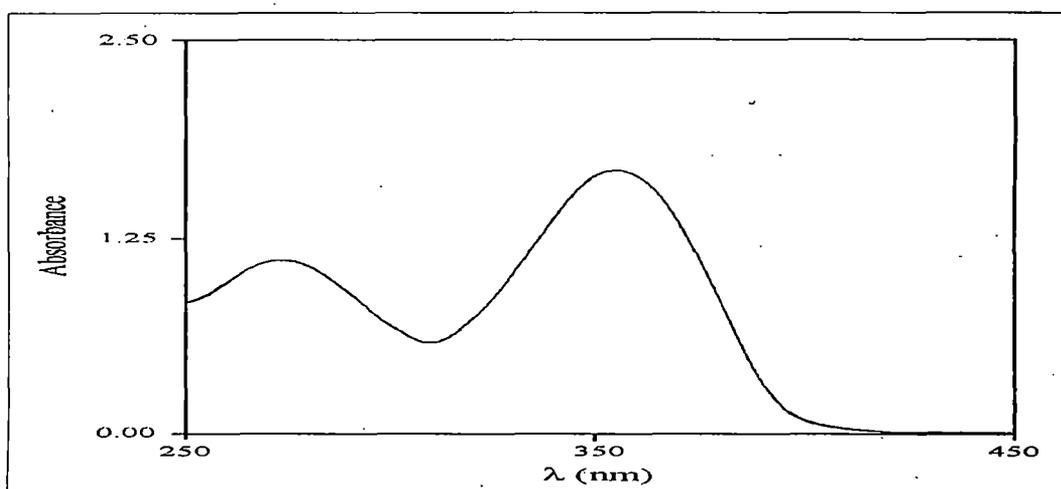


Figure V. 2 Electronic spectrum of 5-13 in dichloromethane.

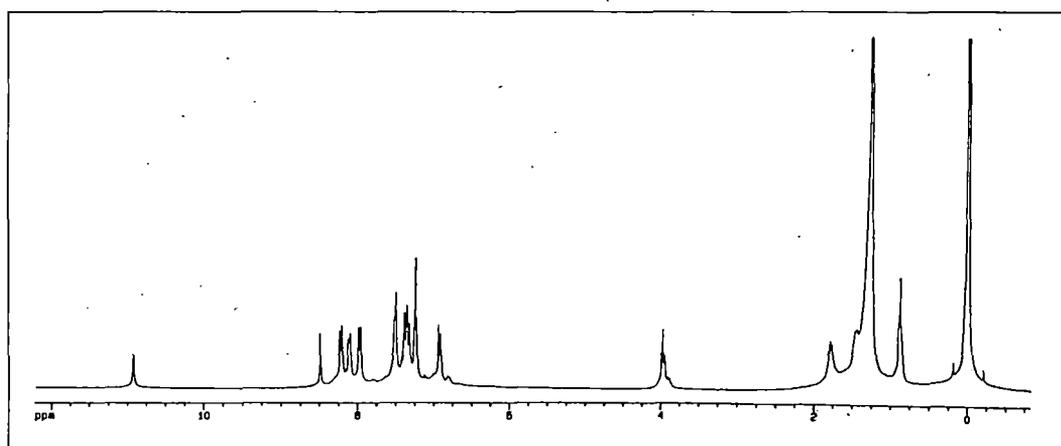


Figure V. 3 ¹H NMR spectrum of 5-13 in CDCl₃.

Table V. 3 Electronic spectroscopic data^a for 5-1 to 5-14.

Comp.	λ nm (ϵ dm ³ mol ⁻¹ cm ⁻¹)	Comp.	λ nm (ϵ dm ³ mol ⁻¹ cm ⁻¹)
5-1	274 (153500), 357 (27600)	5-8	273 (37300), 356 (50800)
5-2	273 (34400), 356 (49300)	5-9	274 (44300), 357 (28100)
5-3	272 (45700), 356 (85100)	5-10	273 (92500), 355 (14500)
5-4	274 (28600), 357 (53000)	5-11	272 (58100), 355 (38700)
5-5	273 (43000), 359 (49800)	5-12	272 (23000), 356 (24000)
5-6	273 (36700), 357 (57400)	5-13	275 (28500), 357 (43600)
5-7	273 (46000), 356 (87400)	5-14	275 (16300), 356 (35500)

^a Solvent: dichloromethane.

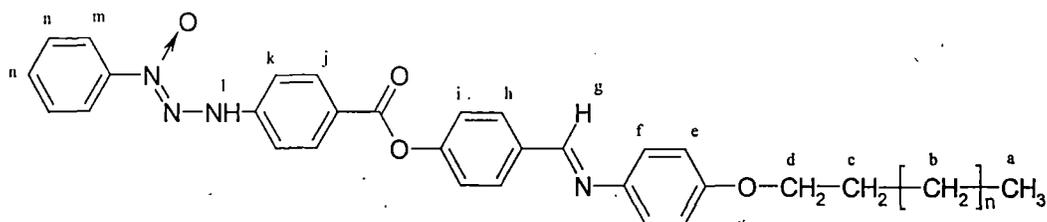
chemical shift of N-H proton remains unaffected by dilution, which indicates the existence of internal hydrogen bonding in solution, as shown in (3). The signal for aldimine proton uniformly appears at ~ 8.5 δ [58] for all the members. The other assignments for the signals of aliphatic and aromatic hydrogen atoms have been made and given in the Table V.4. The chemical shift values (δ , ppm) are all in good agreement with the reported values for the H atoms in similar environment in the other compounds [64, 65].

V. 2. 3. Thermal properties

V. 2. 3. 1 Optical microscopy

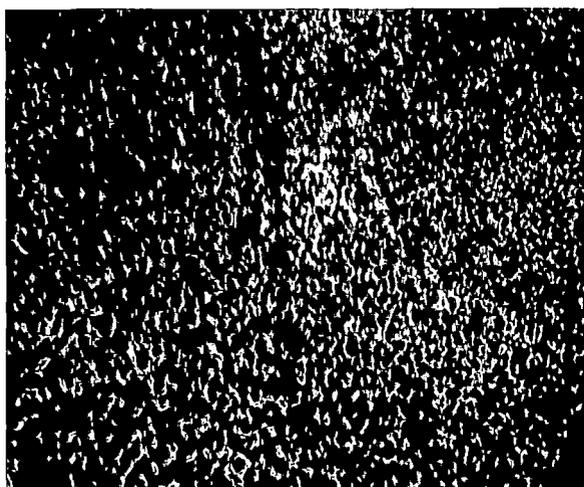
The transition temperatures for compounds 5-1 to 5-14 obtained from the optical microscopic studies have been given in the Table V.5. On the basis of optical microscopy the mesogenic behaviour the compounds of this series may be classified into three groups.

- (i) The first group bears the members 5-1 to 5-6, the compounds of this group melts directly from solid state into nematic phase and finally becomes isotropic at

Table V. 4 ¹H NMR Spectroscopic data^a for compounds 5-1 to 5-14

Comp.	δ (ppm)													
	H ^a	H ^b	H ^c	H ^d	H ^e	H ^f	H ^g	H ^h	H ⁱ	H ^j	H ^k	H ^l	H ^m	H ⁿ
5-1	-	-	-	3.79 s,3H	6.96 d,2H	7.26 d,4H	8.51 s,1H	7.52 d,2H	7.26 d,2H	7.98 d,2H	7.52 m,3H	10.94 s,1H	8.23 d,2H	8.10 m,3H
5-2	-	-	1.48 t,3H	3.94 q,2H	6.95 d,2H	7.26 d,4H	8.50 s,1H	7.53 d,2H	7.26 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.24 d,2H	8.11 m,3H
5-3	-	1.05 t,3H	1.82 m,2H	3.97 t,2H	6.94 d,2H	7.25 d,4H	8.52 s,1H	7.50 d,2H	7.25 d,2H	7.99 d,2H	7.50 m,3H	10.93 s,1H	8.23 d,2H	8.10 m,3H
5-4	0.98 t,3H	1.31 m,14H	1.85 m,2H	3.98 t,2H	6.95 d,2H	7.26 d,4H	8.50 s,1H	7.53 d,2H	7.26 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.24 d,2H	8.11 m,3H
5-5	0.92 t,3H	1.34 m,16H	1.82 m,2H	3.99 t,2H	6.97 d,2H	7.26 d,4H	8.51 s,1H	7.52 d,2H	7.13 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.23 d,2H	8.10 m,3H
5-6	0.90 t,3H	1.33 m,18H	1.83 m,2H	3.91 t,2H	6.98 d,2H	7.26 d,4H	8.51 s,1H	7.52 d,2H	7.26 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.23 d,2H	8.12 m,3H
5-7	0.89 t,3H	1.32 m,8H	1.85 m,2H	3.98 t,2H	6.95 d,2H	7.26 d,4H	8.50 s,1H	7.53 d,2H	7.26 d,2H	8.01 d,2H	7.52 m,3H	10.93 s,1H	8.23 d,2H	8.11 m,3H
5-8	0.89 t,3H	1.30 m,10H	1.84 m,2H	3.98 t,2H	6.95 d,2H	7.26 d,4H	8.51 s,1H	7.52 d,2H	7.13 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.24 d,2H	8.11 m,3H
5-9	0.89 t,3H	1.29 m,12H	1.82 m,2H	3.98 t,2H	6.95 d,2H	7.26 d,4H	8.51 s,1H	7.52 d,2H	7.13 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.24 d,2H	8.12 m,3H
5-10	0.87 t,3H	1.28 m,14H	1.85 m,2H	3.98 t,2H	6.95 d,2H	7.26 d,4H	8.51 s,1H	7.53 d,2H	7.26 d,2H	7.99 d,2H	7.51 m,3H	10.93 s,1H	8.23 d,2H	8.12 m,3H
5-11	0.87 t,3H	1.27 m,16H	1.82 m,2H	3.92 t,2H	7.10 d,2H	7.26 d,4H	8.50 s,1H	7.51 d,2H	7.13 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.23 d,2H	8.11 m,3H
5-12	0.87 t,3H	1.27 m,18H	1.83 m,2H	3.98 t,2H	6.96 d,2H	7.26 d,4H	8.51 s,1H	7.52 d,2H	7.13 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.23 d,2H	8.12 m,3H
5-13	0.87 t,3H	1.27 m,20H	1.80 m,2H	3.98 t,2H	6.94 d,2H	7.26 d,2H	8.50 s,1H	7.53 d,2H	7.24 d,2H	7.98 d,2H	7.37 m,3H	10.93 s,1H	8.24 d,2H	8.12 m,3H
5-14	0.87 t,3H	1.27 m,22H	1.80 m,2H	3.98 t,2H	6.94 d,2H	7.26 d,2H	8.51 s,1H	7.52 d,2H	7.14 d,2H	7.98 d,2H	7.52 m,3H	10.93 s,1H	8.24 d,2H	8.10 m,3H

^a Solvent (CDCl₃); internal standard (SiMe₄)



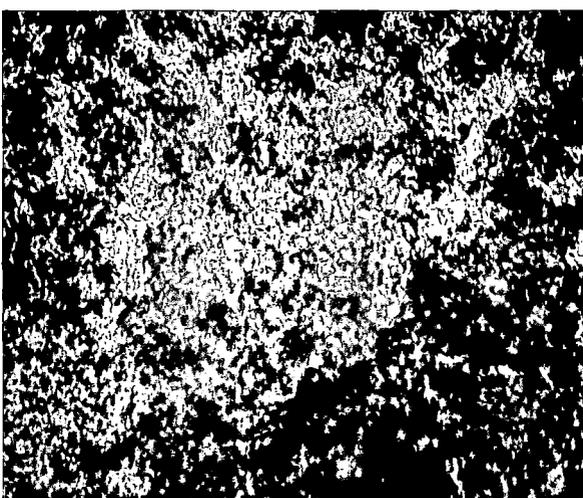
(a)



(b)

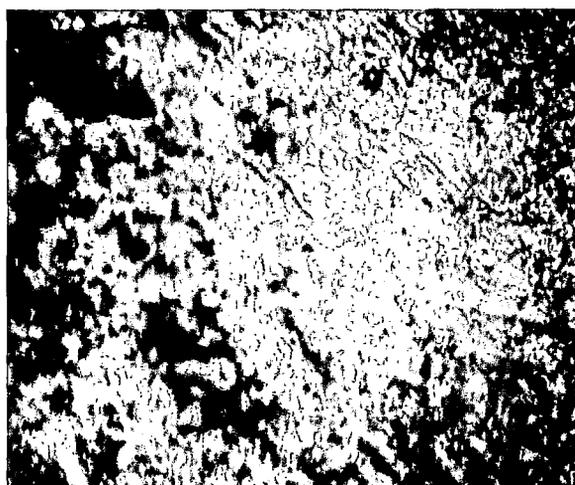


(c)

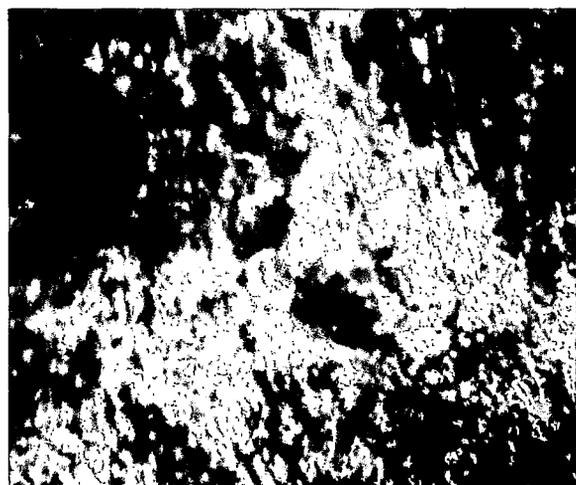


(d)

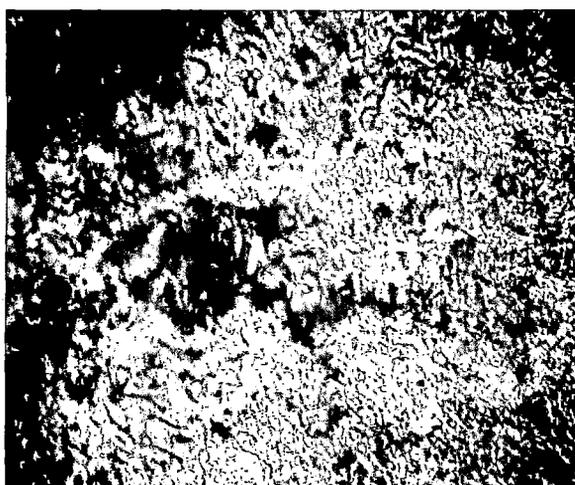
Figure V. 4 Optical texture of compound 5-3 at (a) 102°C during heating, (b) 150°C during heating, (c) 142°C during cooling and (d) 95°C during cooling.



(a)



(b)

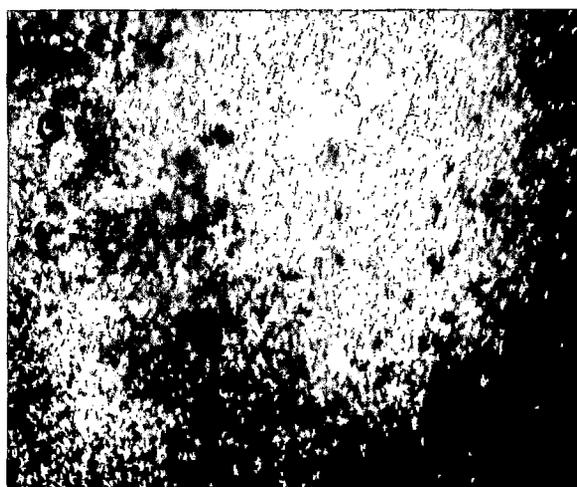


(c)

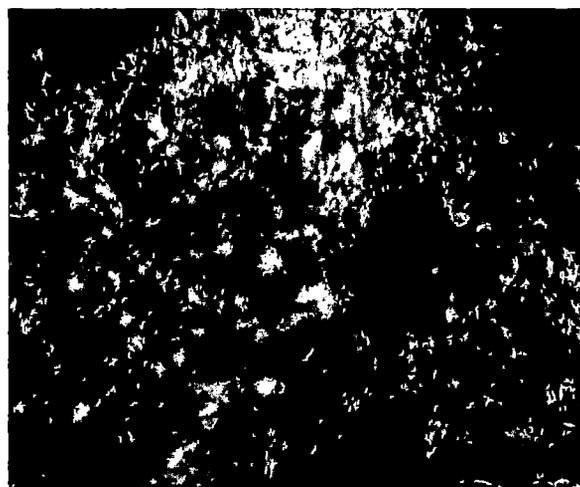


(d)

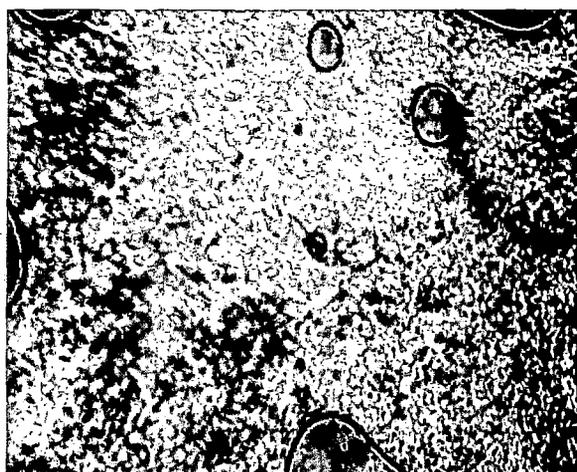
Figure V. 5 Optical texture of compound 5-7 at (a) 95°C during heating, (b) 160°C during heating, (c) 132°C during cooling and (d) 65°C during cooling.



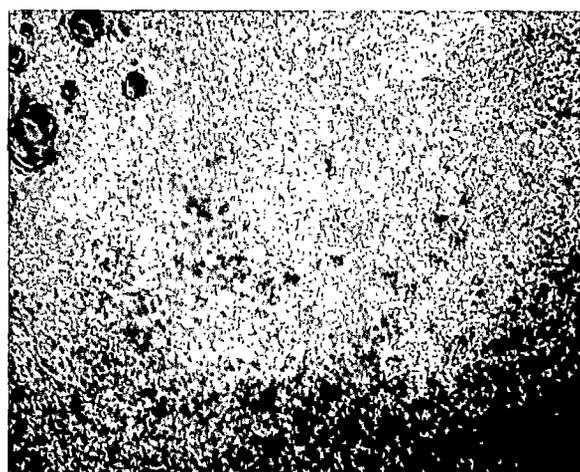
(a)



(b)



(c)



(d)

Figure V. 6 Optical texture of compound 5-14 at (a) 98°C during heating, (b) 158°C during heating, (c) 125°C during cooling and (d) 85°C during cooling.

higher temperature (165-180°C), on cooling the nematic phase reappears at temperature few degree below the clearing temperature (Fig. V.4). The nematic phase continues up to the solidification temperature for all the compounds of this group.

- (ii) The second group is the group of the members 5-7 to 5-9, here the compounds melts to the smectic phase which on further heating transforms into the nematic liquids (Fig. V.5). The nematic phase finally disappears at the clearing temperature. During cooling the nematic phase reappears and continues up to the solidification temperature without any appearance of smectic phase.
- (iii) The compounds 5-10 to 5-14 melt into the smectic phase and become isotropic at the higher temperature without entering to the nematic phase. On reversal cooling the smectic phase reappears and continues up to the solidification temperature (Fig. V.6).

The variation of melting point (T_m) and mesophase-isotropic transition temperature (T_{mi}) with the number of carbon atoms (n) in the alkoxy chains of compound (5) is shown in Fig. V.7. Here the odd-even effect on transition temperature is absent. The melting point (T_m) gradually decreases from $n=1$ to $n=4$ then increases slowly from $n=6$ to $n=13$. The mesomorphic temperature range for $n=9$ is minimum within the series.

The variation of transition temperature from isotropic to mesophase (T_{Im}) and the crystallization temperature (T_{Cr}) with the number of carbon atoms (n) of alkoxy chains are shown in Fig. V.8. On cooling the members show the similar pattern of variation of phase transition temperature as that of heating.

Table V. 5. Transition temperatures ($^{\circ}\text{C}$) obtained from optical microscopic study and the enthalpy changes (kJ mol^{-1}) observed in the DSC measurement for 5-1 to 5-14

Comp.	R	Cr	S		N		I	
			Heating (ΔH)	Cooling (ΔH)	Heating (ΔH)	Cooling (ΔH)	Heating (ΔH)	Cooling (ΔH)
5-1	CH_3	•	$95.55^{\circ}\text{C}^{\text{a}}$	–	•	$159.65^{\circ}\text{C}^{\text{a}}$	•	
		•	$89.25^{\circ}\text{C}^{\text{a}}$	–	•	$154.36^{\circ}\text{C}^{\text{a}}$	•	
5-2	C_2H_5	•	$85.64^{\circ}\text{C}^{\text{a}}$	–	•	$174.85^{\circ}\text{C}^{\text{a}}$	•	
		•	$82.35^{\circ}\text{C}^{\text{a}}$	–	•	$169.40^{\circ}\text{C}^{\text{a}}$	•	
5-3	C_3H_7	•	$72.45^{\circ}\text{C}^{\text{a}}$	–	•	$162.55^{\circ}\text{C}^{\text{a}}$	•	
		•	$63.25^{\circ}\text{C}^{\text{a}}$	–	•	$159.50^{\circ}\text{C}^{\text{a}}$	•	
5-4	C_4H_9	•	$67.46^{\circ}\text{C}^{\text{a}}$	–	•	$159.62^{\circ}\text{C}^{\text{a}}$	•	
		•	$59.84^{\circ}\text{C}^{\text{a}}$	–	•	$157.35^{\circ}\text{C}^{\text{a}}$	•	
5-5	C_5H_{11}	•	$70.43^{\circ}\text{C}^{\text{a}}$	–	•	$173.34^{\circ}\text{C}^{\text{a}}$	•	
		•	$65.20^{\circ}\text{C}^{\text{a}}$	–	•	$170.50^{\circ}\text{C}^{\text{a}}$	•	
5-6	C_6H_{13}	•	$65.50^{\circ}\text{C}^{\text{a}}$	–	•	$168.36^{\circ}\text{C}^{\text{a}}$	•	
		•	$62.45^{\circ}\text{C}^{\text{a}}$	–	•	$164.30^{\circ}\text{C}^{\text{a}}$	•	
5-7	C_7H_{15}	•	68.53°C (6.88)	•	120.19°C (1.32)	•	161.00°C (1.71)	•
		•	$58.40^{\circ}\text{C}^{\text{a}}$	–	•	156.66°C (0.25)	•	
5-8	C_8H_{17}	•	70.34°C (20.31)	•	124.40°C (1.66)	•	175.70°C (1.57)	•
		•	$52.35^{\circ}\text{C}^{\text{a}}$	–	•	160.42°C (1.99)	•	
5-9	C_9H_{19}	•	78.27°C (15.71)	•	119.49°C (1.45)	•	143.94°C (0.76)	•
		•	54.57°C (8.23)	–	•	142.06°C (1.15)	•	

(Continued)

Table V. 5. (Continued)

Comp.	R	Cr	S		N		I
			Heating (ΔH) Cooling (ΔH)	Heating (ΔH) Cooling (ΔH)	Heating (ΔH) Cooling (ΔH)		
5-10	C ₁₀ H ₂₁	•	79.04°C (18.09)	•	–	187.49°C ^a	•
		•	47.32°C (7.36)	•	–	175.86°C (2.33)	•
5-11	C ₁₁ H ₂₃	•	85.07°C (18.64)	•	–	177.86°C (1.09)	•
		•	58.57°C (9.57)	•	–	174.72°C (0.67)	•
5-12	C ₁₂ H ₂₅	•	85.79°C (20.39)	•	–	176.25°C ^a	•
		•	59.72°C (13.83)	•	–	176.22°C (3.28)	•
5-13	C ₁₃ H ₂₇	•	95.35°C (21.94)	•	–	163.5°C ^a	•
		•	76.43°C (12.60)	•	–	162.32°C (0.17)	•
5-14	C ₁₄ H ₂₉	•	91.82°C (16.08)	•	–	174.30°C ^a	•
		•	69.78°C (17.68)	•	–	173.33°C (0.50)	•

^a Transition temperature observed only in optical microscopy, not detected by DSC.

V. 2. 3. 2 Differential Scanning Calorimetry

The enthalpies for different phase transitions detected by differential scanning calorimetric study have been given within the braces in Table V.5. One representative DSC thermogram of compound 5-10 has been shown in Fig. V.9. The enthalpy change for the solid to mesophase (smectic or nematic) transitions is in the range 5-21 kJ mol⁻¹. The amount of enthalpy change for the smectic to nematic phase transition is in the range 1-2 kJ mol⁻¹ and the clearing enthalpy (nematic or smectic to isotropic) is in the range 0.1-3.28 kJ mol⁻¹.

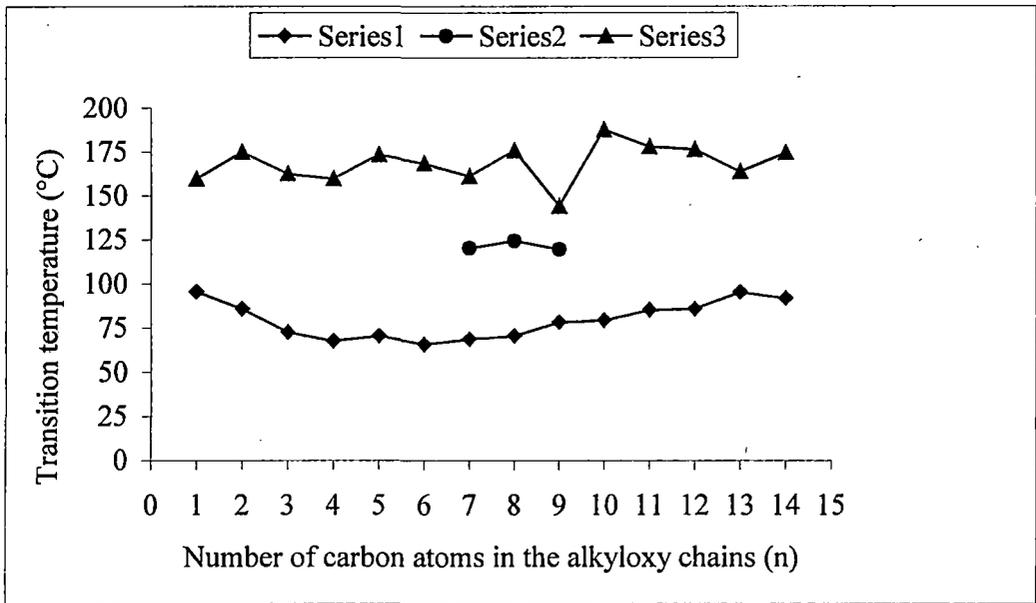


Figure V. 7 Variation of transition temperatures with the number of carbon atoms present in the alkoxy chain during heating. (Series1→ solid to mesophase (T_m), Series2→ smectic to nematic and series3→mesophase to isotropic transitions)

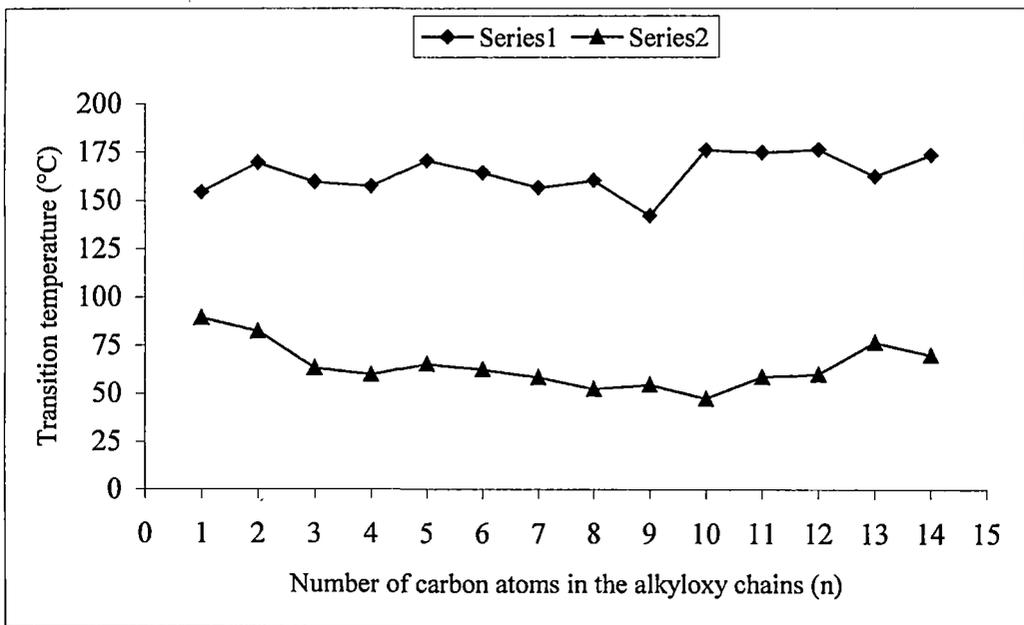
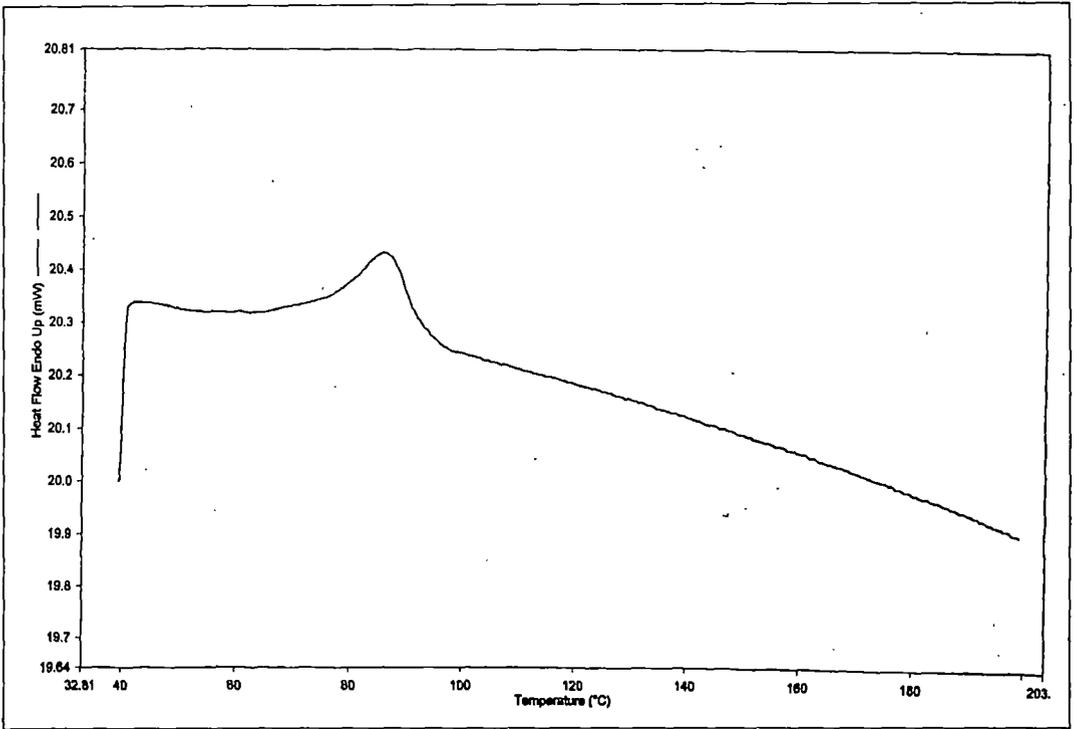
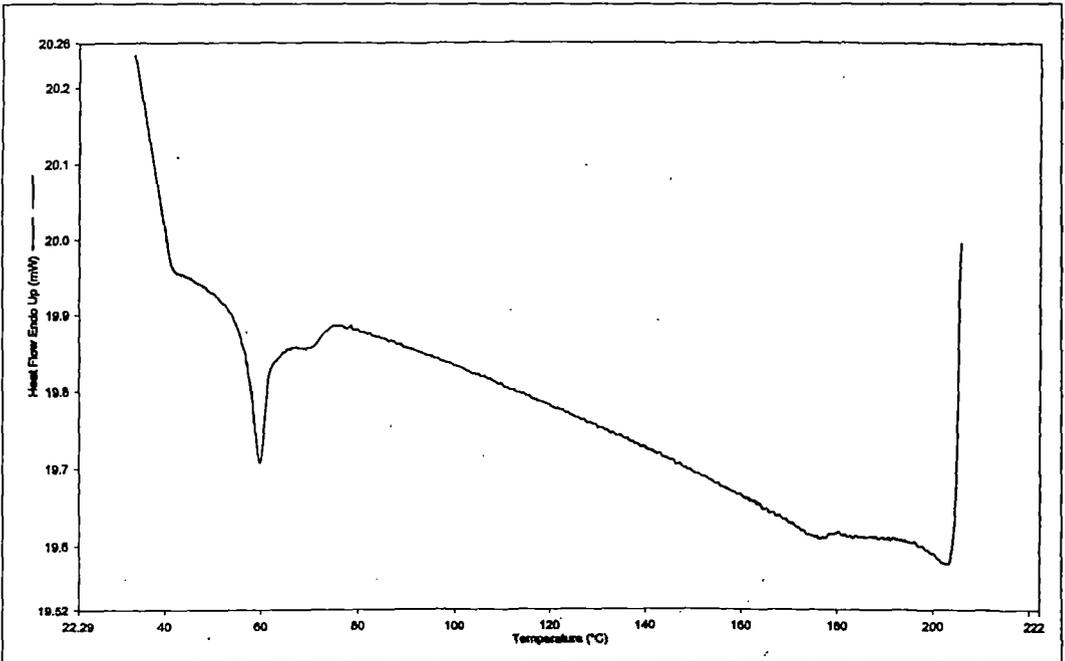


Figure V. 8 Variation of transition temperatures with the number of carbon atoms present in the alkoxy chain during cooling. (Series1→ isotropic to nematic and series2→ nematic to solid transitions)



(a)



(b)

Figure V. 9 DSC traces for 5-12 (a) during heating and (b) during cooling.

V. 2. 3. 3 *Small angle X-ray diffraction analysis*

The small angle X-ray diffraction analysis for the confirmation of the existence of the mesophase has been done for two members (5-9 and 5-14) of the above series of compounds. The X-ray diffraction photograph was taken at room temperature for 5-9 in the solid state and has been shown in Figure V.10. Our attempt to align both the samples by applied magnetic field met with failures, due to the limitation of our experimental setup. We have taken the X-ray diffraction photographs for 5-9 at 90°C and 100°C and for 5-14 at 95°C. The X-ray diffraction photographs of 5-9 & 5-14 taken in the mesophase have been shown in Figure V.11.

V. 2. 4 *Conclusions*

- (i) In our endeavor to incorporate mesogenic behaviour in 1-phenyl-3-phenyltriazene-1-oxide systems, a new series of compounds has been designed. The objective was to include two additional phenyl rings as rigid cores linked by two functional groups flanked by a terminal n-alkoxy group within the 1-phenyl-3-phenyltriazene-1-oxide system. Here we have used four phenyl rings linked by one triazene-1-oxide, one ester and one aldimine groups with a terminal n-alkoxy group. A new homologous series of 1-phenyl-3-phenyltriazene-1-oxide compounds, 3-(4'-(4''-imino(4'''-(n-alkoxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide, has been successfully synthesized.
- (ii) The compounds have been characterized on the basis of their spectral (IR, NMR and electronic) data.

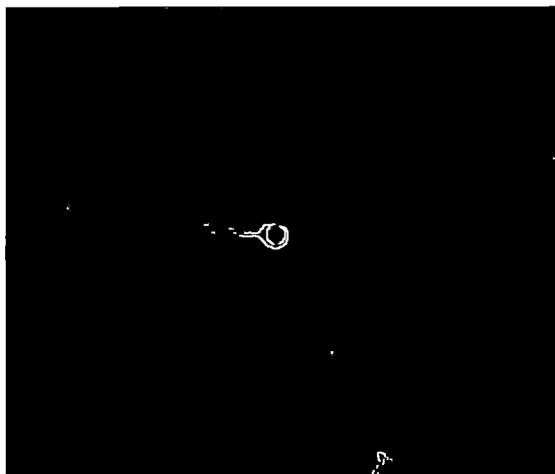
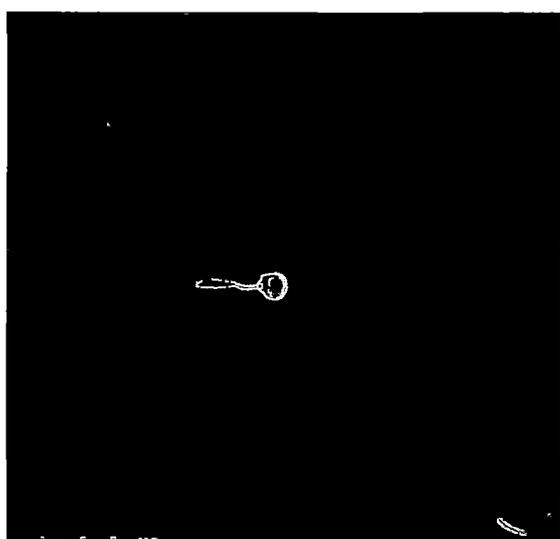


Figure V. 10 X-ray diffraction photograph of 5-9 at room temperature in the solid state.



(a)



(b)

Figure V. 11 X-ray diffraction photograph of (a) 5-9 at 90°C and (b) 5-14 at 95°C.

- (iii) All the members of this family show thermotropic mesogenic behaviour over a good temperature range.
- (iv) The mesogenic behaviour of compounds (5) is dependent on the length of the alkoxy chain. The compounds (5-1 to 5-6) of this new series with show nematic phase. The compounds (5-7 to 5-9) exhibit smectic phase on melting followed by nematic phase. Compounds 5-10 to 5-14 exhibit only smectic phase.
- (v) The enthalpy changes of the compounds 5-7 to 5-14 on phase transitions have been measured by DSC.

V. 3. Experimental

V. 3. 1 *Preparation of compounds*

V. 3. 1. 1 *Chemicals*

4-Hydroxybenzoic acid, *p*-hydroxybenzaldehyde, 4-aminobenzoic acid, sodium nitrite, sodium acetate were purchased from E. Merck Ltd., India and were used without further purification.

V. 3. 1. 2 *Synthesis of 3-(4'-carboxylatophenyl)-1-phenyltriazen-1-oxide*

3-(4'-Carboxylatophenyl)-1-phenyltriazen-1-oxide has been prepared following a reported method [62]. In this method an aqueous ethanolic solution of freshly prepared phenylhydroxyl amine was stirred mechanically with a sufficient quantity of crushed ice to keep the temperature at $\sim 0^{\circ}\text{C}$. Then a solution of 4-carboxylatobenzene diazonium chloride was added slowly to the above reaction mixture (1:1 molar ratio) with vigorous stirring. The pH of the reaction medium was kept at ~ 5.0 by the

addition of saturated solution of sodium acetate. The precipitate of 4'-carboxylatotriazene-1-oxide gradually separated out. It was collected by filtration and finally recrystallised from a mixture of ethanol and acetone (1:1 v/v). (Yield: 2.5 g; *ca.* 48 %).

V. 3. 1. 3 *Synthesis of 3-(4'-(4"-formyl-phenyl)carboxylatophenyl)-1-phenyl-triazene-1-oxide*

The compound has been prepared by esterification of 3-(4'-Carboxylatophenyl)-1-phenyltriazene-1-oxide with *p*-hydroxybenzaldehyde. The esterification was made following a reported method [59]. A mixture of 3-(4'-Carboxylatophenyl)-1-phenyl-triazene-1-oxide (0.51 g; 2 mmol), dicyclohexyl carbodiimide (DCC) (0.41 g; 2 mmol), *p*-hydroxybenzaldehyde (0.24 g; 2 mmol) and dimethylaminopyridine (DMAP) (0.02 g; 0.2 mmol) in the mole ratio 1:1:1:0.1 were taken in dichloromethane (25 mL) and the mixture was stirred at room temperature for 24 hrs. The reaction mixture was filtered and the filtrate was collected. Evaporation of solvent produced a mixture of compounds. 3-(4'-(4"-formyl-phenyl)carboxylatophenyl)-1-phenyl-triazene-1-oxide was isolated by recrystallisation from aqueous ethanol (Yield: 0.65 g; *ca.* 89 %).

V. 3. 1. 4 *Synthesis of 4-(n-alkyloxy)nitrobenzene*

4-Alkyloxynitrobenzenes were prepared following the method of Williamsons ether synthesis. The preparative method has been described earlier in Chapter III. Section III.3.1.

V. 3. 1. 5 *Synthesis of 4-(n-alkyloxy)aniline*

4-Alkyloxy anilines were prepared following a reported method [59]. The synthesis of 4-(n-octyloxy)aniline has been discussed below as representative case.

To a suspension of one equivalent of 4-(n-octyloxy)nitrobenzene (0.50 g, 2 mmol) in ethanol (100 mL, absolute) were added five equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.26 g, 10 mmol). The mixture was refluxed for 6 hrs, cooled to room temperature and poured onto ice. The pH was adjusted to 8 using NaOH (2 mol L^{-1}) and the colourless mixture was extracted with ethyl acetate (200 mL). The ethyl acetate layer was dried over anhydrous MgSO_4 and evaporated under reduced pressure. The solid was crystallized from an ethanol-water mixture (4:1 v/v), filtered and vacuum dried. The 4-(n-octyloxy)aniline was collected as a whitish solid after recrystallization from ethanol. (Yield: 0.23 g; ca. 52 %).

V. 3. 1. 6 *Synthesis of 3-(4'-(4''-imino(4'''-(n-alkyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazen-1-oxide*

All the compounds have been prepared by condensation between 3-(4'-(4''-formyl-phenyl)carboxylatophenyl)-1-phenyltriazen-1-oxide and 4-(n-alkyloxy)aniline. The condensation was made following reported method [66] for the preparation of imines, the synthesis of 3-(4'-(4''-imino(4'''-(n-octyloxy)phenyl)phenyl)carboxylatophenyl)-1-phenyl-triazen-1-oxide has been given as a representative case.

A mixture of 3-(4'-(4''-formyl-phenyl)carboxylatophenyl)-1-phenyltriazen-1-oxide (0.72 g, 2 mmol) and 4-(n-octyloxy)aniline (0.47 g, 2 mmol) was taken in 50 ml dry alcohol along with few drops of acetic acid and was refluxed for 5 hrs. The reaction mixture was then cooled to room temperature and kept overnight at room

temperature. The solid deposited by this time was filtered off. The solid was repeatedly washed by ethanol (5 x 10 ml). The 3-(4'-(4''-imino(4'''-(n-octyloxy)-phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide was then recrystallized from a mixture of dichloromethane and ethanol (1:5 v/v). Analytically pure compound was obtained by repeated recrystallization. (Yield: 0.77 g; *ca.* 66 %).

V. 3. 2 Characterization of compounds

All the compounds were characterized by C, H and N microanalysis. The microanalysis data of all the compounds (Table V. 5) are in good agreement with the proposed compositions.

Table V. 5 Microanalysis data for compounds 5-1 to 5-14.

Compound	Carbon %		Hydrogen %		Nitrogen %	
	Calculated	Found	Calculated	Found	Calculated	Found
5-1	69.53	69.58	4.72	4.75	12.02	12.06
5-2	70.00	70.08	5.00	5.04	11.67	11.62
5-3	70.45	70.39	5.26	5.21	11.34	11.30
5-4	70.87	70.81	5.51	5.53	11.02	11.05
5-5	71.26	71.29	5.75	5.78	10.73	10.74
5-6	71.64	71.71	5.97	5.95	10.45	10.41
5-7	72.00	71.98	6.18	6.17	10.18	10.21
5-8	72.34	72.36	6.38	6.37	9.93	9.91
5-9	72.66	72.61	6.57	6.52	9.69	9.67
5-10	72.97	72.93	6.76	6.72	9.46	9.49
5-11	73.27	73.34	6.93	6.97	9.24	9.27
5-12	73.55	72.51	7.09	7.06	9.03	9.07
5-13	73.82	73.85	7.25	7.23	8.83	8.81
5-14	74.07	74.13	7.41	7.43	8.64	8.67

V. 3. 3 *Physical measurements*

(i) *Infrared spectra*

IR spectra were recorded on Shimadzu FT-IR 8300 spectrometer as KBr disc.

(ii) *Electronic spectra*

Electronic spectra were obtained on Shimadzu 240 spectrophotometer.

(iii) *NMR spectra*

Described in Chapter III, Section III.3.3. (iii).

(iv) *Elemental analysis*

Described in Chapter III, Section III.3.3.(v).

(v) *Polarized Optical microscopy*

Described in Chapter III, Section III.3.3. (vi).

(vi) *Differential Scanning Calorimetry (DSC)*

Differential Scanning Calorimetric measurements were done using Pyris-6 Differential Scanning Calorimeter.

(vii) *Small angle X-ray Diffraction*

Described in Chapter III, Section III. 3. 3. (vii).

References

1. E. Bamberger and Hr. Busdorf, *Ber dt chem Ges*, **29**, 103 (1896); **33**, 3510 (1900).
2. E. Bamberger and A. Stiegelmann, *Ber dt chem Ges*, **32**, 3554 (1899).
3. E. Bamberger and E. Renauld, *Ber dt chem Ges*, **29**, 104 (1896); **30**, 2278 (1897).
4. N.L. Gebhard and H.B. Thompson, *J chem Soc*, **95**, 771 (1909).
5. M. Elkins and L. Hunter, *J chem Soc*, 1346 (1938).
6. S.B. Sarkar, M. Khalil, S.C. Saha and S.K. Talapatra, *Acta. Cryst.* **C39**, 1075 (1983).
7. R.L. Dutta and R. Sharma, *J. Sci. Ind. Res.*, **40**, 715 (1981).
8. C.K. Pal, P. Chakraborty, A. Chakravorty, *Indian J. Chem.*, **40A**, 675 (2001).
9. Z. Ciunik, J.A. Wolny, M.F. Rudolf, S. Wolowiec, *J. Chem. Soc. Dalton Transactions*, 885 (2002).
10. S. Karmakar, S.B. Choudhury, D. Ray, A. Chakravorty, *Polyhedron* **12**, 2325 (1993).
11. S. Karmakar, S.B. Choudhury, D. Ray, A. Chakravorty, *Polyhedron* **12**, 291 (1993).
12. S. Pattanayak, P. Chakraborty, S. K. Chandra, A. Chakravorty, *Polyhedron* **15**, 1121 (1996).
13. R.N. Mukherjee, O.A. Rajan, A. Chakravorty, *Inorg. Chem.* **21**, 785 (1982).
14. F.M. Rudolf, J.A. Wolny, T. Lis, P. Starynowicz, *J. Chem. Soc. Dalton Trans.*, 1972 (1992).

15. F.M. Rudolf, Z. Ciunik, K. Gatner, J.A. Wolny, *Polyhedron* **11**, 2591 (1992).
16. H. Aneetha, J. Padmaja, P.S. Zacharias, *Polyhedron*, **15**, 2445 (1996).
17. S.C. Saha, D. Chakravorty and P. Chakravorty, *Indian J chem*, **15A**, 816 (1977).
18. P.D. Chatlangya, C.S. Bhandari and N.C. Sogani, *J Indian chem Soc*, **54**, 1001 (1977).
19. A. Guha Thakurta, B. Das and S.C. Shome, *J Indian chem Soc*, **56**, 321 (1979).
20. N.C. Sogani and S.C. Bhattacharya, *Analyt Chem*, **29**, 397 (1957).
21. U.C. Durgapal and N.C. Sogani, *J Indian chem Soc*, **35**, 542 (1958).
22. H.K.L. Gupta and N.C. Sogani, *J Indian chem Soc*, **36**, 87 (1959).
23. U.C. Durgapal and N.C. Sogani, *J Indian chem Soc*, **36**, 263 (1959).
24. U.C. Durgapal and N.C. Sogani, *J Indian chem Soc*, **35**, 842 (1958).
25. H.K.L. Gupta and N.C. Sogani, *J Indian chem Soc*, **37**, 97 (1960).
26. R.N. Mathur and N.C. Sogani, *J Indian chem Soc*, **37**, 117 (1960).
27. S. Mehra and N.C. Sogani, *J Indian chem Soc*, **37**, 562 (1960).
28. G. Mehra and N.C. Sogani, *J Indian chem Soc*, **39**, 145 (1962).
29. S.M. Dugar, D.N. Purohit and N.C. Sogani, *J Indian chem Soc*, **40**, 213 (1963).
30. S.M. Dugar, D.N. Purohit and N.C. Sogani, *J Indian chem Soc*, **40**, 667 (1963).
31. A.K. Majumdar and S.C. Saha, *Analytica chim Acta*, **44**, 85 (1969).
32. A.K. Majumdar and D. Chakravorty, *Analytica chim Acta*, **53**, 127 (1971).
33. A.K. Majumdar and D. Chakravorty, *Z analyt Chem*, **257**, 33 (1971).
34. A.K. Majumdar and D. Chakravorty, *Analytica chim Acta*, **53**, 393 (1971).
35. D. Chakravorty, *Analytica chim Acta*, **70**, 207 (1974).
36. S.C. Shome, H.R. Das and B. Das, *Analytica Chem*, **38**, 1522 (1966).
37. B. Das and S.C. Shome, *Talanta*, **17**, 75 (1970).

38. J.P.C. Jamini, D.N. Purohit and N.C. Sogani *Z. Analyt. Chem.*, **203**, 181 (1964).
39. A.K. Majumdar and D. Chakravorti, *Analytica Chim Acta*, **55**, 450 (1971).
40. A.K. Majumdar, B.C. Bhattacharya and B.C. Ray, *Analytica chim Acta*, **57**, 425 (1971).
41. N.R. Biswas, B.C. Ray and S. Lahiri, *J Indian chem Soc*, **56**, 473 (1979).
42. H.K.L. Gupta, T.C. Jain and N.C. Sogani, *J Indian chem Soc*, **31**, 531 (1960).
43. A.K. Majumdar, S.C. Saha, *Analytica chim Acta*, **40**, 299 (1968).
44. N.C. Sogani, S.C. Bhattacharya, *Analyt Chem*, **28**, 81 (1956).
45. N.C. Sogani, S.C. Bhattacharya, *Analyt Chem*, **28**, 1616 (1956).
46. H.K.L. Gupta and N.C. Sogani, *J Indian chem. Soc*, **38**, 771 (1961).
47. S.M. Dugar, D.N. Purohit, and N.C. Sogani, *J Indian chem Soc*, **43**, 703 (1966).
48. D. Chakravorty and A.K. Majumdar, *J Indian chem Soc*, **54**, 258 (1977).
49. D.N. Purohit, *Talanta*, **14**(3), 353 (1967).
50. J. L. Miesel, Eli Lilly & Co., USA, US Patent 74-503580 19740906, USA, (1976).
51. K. Vaughan, L.M. Cameron, S. Christie and M., J. Zaworotko, *Acta Cryst.*, **C48**, 1985 (1992).
52. D.E.V. Wilman, *Proceedings of the 3rd International Symposium on the Biological Oxidation of Nitrogen in Organic Molecules*, edited by J.W. Gorrod & L.A. Damani, p-297-302, (1985), Chichester; Ellis Horwood.
53. D.E.V. Wilman and P.M. Goddard, *Prog. Pharmacol. Clin. Pharmacol.* **8**, 335 (1991).
54. T. Mitsuhashi and O. Simamura, *J. Chem. Soc. (B)*, **4**, 705 (1970).

55. T. Mitsuhashi, Y. Osamura and O. Simamura, *Tetrahedron Lett*, **30**, 2593 (1965).
56. C.V. Yelamaggad, I. Shashikala, D.S.S. Rao and S.K. Prasad, *Liquid Crystals*, **31**, 1027 (2004).
57. L. Douce, T.H. Diep, R. Ziessel, A. Skoulios and M. Cesario, *J. Mater. Chem.*, **13**, 1533 (2003).
58. C.V. Yelamaggad, I. Shashikala, D.S.S. Rao and S.K. Prasad, *Liquid Crystals*, **31**, 1027 (2004).
59. S. Morrone, G. Harrison and D.W. Bruce, *Adv. Matter.* **7**, 665 (1995)
60. A.D. Cross and R.A. Jones, *An introduction to practical infrared spectroscopy*, Butterworth and Co (publishers) Ltd. London, (1969).
61. A Vinciguerra, P.G. Simpson, Y. Kakinti and J.V. Quagliano, *Inorg. Chem.*, **2**, 286 (1963).
62. N.C. Sogani and S.C. Bhattacharyya *J. Indian Chem. Soc.* **36**, 563 (1959).
63. A. Chakravorty, B. Behera and P.S. Zacharias, *Inorg. Chim. Acta*, **2**(1), 85 (1968).
64. Z. Hou, Y. Fujiwara and H. Taniguchi, *J. Org. Chem.*, **53**, 3118, (1988).
65. D.W. Bruce and J.P. Rourke, *Polyhedron*, **14**, 1915, (1995).
66. R.V. Deun and K. Binnemans, *Liquid Crystals*, **30**, 479 (2003).