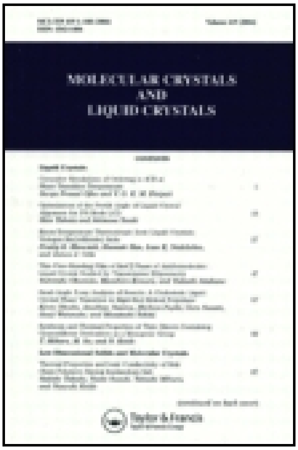

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Synthesis and Liquid Crystalline Properties of Novel Triazene-1-oxide Derivatives

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Synthesis and Liquid Crystalline Properties of Novel Triazene-1-oxide Derivatives

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A new group of compounds, C_6H_5-N(O)=N-NH-C_6H_4-C(O)-O-C_6H_4-CH=N-C_6H_4-OR, *(**1**), [R = n-alkyl group; **1a** (R =* C_7H_{15} *) to **1h** (R =* $C_{14}H_{29}$*)], has been designed and synthesized to develop triazene-1-oxide based liquid crystals. All the compounds have been characterized on the basis of their spectral data. Their thermal behavior has been examined and found to exhibit thermotropic liquid crystalline behavior over a wide range of temperature. All members of this family uniformly show nematic phase behavior on melting up to the clearing point during heating as well as on phase entering up to the solidification during cooling. An odd–even effect on transition temperatures has been observed during heating as well as cooling.*

Keywords: ester; imine; liquid crystal; nematic; triazene-1-oxide

INTRODUCTION

Triazene-1-oxides and their derivatives [1,2] provide a flexible ligand frame and are well known for their metal binding properties [3–12]. They offer wide varieties of stereochemistry to different metal ions [3,4]. Triazene-1-oxide derivatives have also been found to exhibit biological activities [13–15]. But no report on mesogenic properties of triazene-1-oxides is available in the literature, despite the fact that extensive studies on mesogenic behavior of aryldiazene-1-oxides have been done [16–19]. The flexible frame of triazene-1-oxides prompted us

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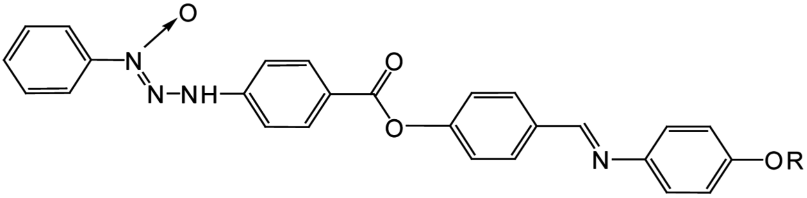
to design a new group of triazene-1-oxides with the potential to exhibit liquid crystalline properties.

Herein we wish to report the synthesis, characterization, and mesogenic behavior of a new group of triazene-1-oxide (**1**) having two additional phenyl rings as core groups linked via ester and imine functional groups.



(**1**)

EXPERIMENTAL SECTION

Measurements

Infrared spectra were recorded by JASCO 5300 FT-IR spectrometer. Electronic spectra were obtained using Perkin Elmer Lambda 2S spectrophotometer. ^{1}H NMR spectra were recorded on Bruker DPX 300 spectrometer. Microanalyses (C, H, N) were performed using an Elementan Vario EL III Carlo Erban 1108 elemental analyzer at CDRI, Lucknow, India. Optical microscopic study at different temperatures was done using a polarizing microscope (Manufacturer: Labex K. K. International, India; Model: Co ax 10B(POL, 150X). The probe temperature was controlled using Metler FP 80 control system and FP82 hot stage.

Synthesis

n-Alkyl bromides, nitro benzene, 4-hydroxyaniline, 4-hydroxybenzaldehyde, 4-aminobenzoic acid, sodium nitrite, ammonium chloride, sodium acetate and zinc powder were purchased from E. Merck Ltd., India and were used without further purification.

Synthesis of 3-(4′-Carboxylatophenyl)-1-phenyltriazene-1-oxide

3-(4′-Carboxylatophenyl)-1-phenyltriazene-1-oxide has been synthesized by coupling 4-carboxylatophenyldiazoniumchloride with *β*-phenylhydroxylamine following a procedure reported by Sogani and Bhattacharya [2]. The product was finally recrystallized from a mixture of ethanol and acetone (1:1 v/v). Yield: 48%.

Synthesis of 3-(4′-(4″-Formylphenyl)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 [20]. 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. 3-(4′-(4″-Formylphenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide was isolated by recrystallization from aqueous ethanol. Yield: 0.65 g, 89%.

Synthesis of 4-(n-Alkyloxy)nitrobenzene

4-Alkyloxynitrobenzenes were prepared following a reported method [21]. The 4-(*n*-alkyloxy)nitrobenzenes were collected either as pale yellow liquid or pale yellow solid (C10–C14) after the complete removal of the solvent. Yield: 85%.

Synthesis of 4-(n-Alkyloxy)aniline

4-Alkyloxyanilines were prepared following a general method [20]. The 4-(*n*-alkyloxy)anilines were collected as a whitish solid after recrystallization from ethanol.

Synthesis of 3-(4′-(4″-Imino(4‴-(n-alkyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide

All the compounds have been prepared by condensation between 3-(4′-(4″-formyl-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide and 4-(*n*-alkyloxy)aniline. The condensation was made following reported method [22] for the preparation of imines, the synthesis of 3-(4′-(4″-imino(4‴-(*n*-octyloxy)phenyl)phenyl)carboxylatophenyl)-1-phenyl-triazene-1-oxide has been given as a representative case.

A mixture of 3-(4′-(4″-formylphenyl)carboxylatophenyl)-1-phenyl-triazene-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 × 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, 66%.

The other compounds of this series were obtained using same procedure as that of 3-(4′-(4″-imino(4‴-(*n*-octyloxy)phenyl)phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide. The characterization data for **1a** to **1h** of this homologous series are summarized as follows.

3-(4′-(4″-Imino(4‴-(n-heptyloxy)phenyl)phenyl)-carboxylatophenyl)-1-phenyltriazene-1-oxide, [1a]

Yield: 63%. Anal. Calcd for $C_{33}H_{34}N_4O_4$: C, 72.00; H, 6.18; N, 10.18; found: C, 71.98; H, 6.17; N, 10.21; mp: 68.53°C; IR (KBr cm^{-1}) 3213 m, 1740 s, 1605 s, 1504 s, 1469 s, 1423 m, 1307 m, 837 s, 813 w; UV-VIS nm (ε dm^3 mol^{-1} cm^{-1}) 273(46000), 356(87400); ^{1}H NMR (300 MHz, $CDCl_3$): 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).

3-(4′-(4″-Imino(4‴-(n-octyloxy)phenyl)phenyl)-carboxylatophenyl)-1-phenyltriazene-1-oxide, [1b]

Yield: 66%. Anal. Calcd for $C_{34}H_{36}N_4O_4$: C, 72.34; H, 6.38; N, 9.93; found: C, 72.36; H, 6.37; N, 9.91; mp: 70.34°C; IR (KBr cm^{-1}) 3247 m, 1736 s, 1605 s, 1504 s, 1474 s, 1419 m, 1319 m, 837 s, 813 w; UV-VIS nm (ε dm^3 mol^{-1} cm^{-1}) 273(37300), 356(50800); ^{1}H NMR (300 MHz, $CDCl_3$): 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).

3-(4′-(4″-Imino(4‴-(n-nonyloxy)phenyl)phenyl)-carboxylatophenyl)-1-phenyltriazene-1-oxide, [1c]

Yield: 68%. Anal. Calcd for $C_{35}H_{38}N_4O_4$: C, 72.66; H, 6.57; N, 9.69; found: C, 72.61; H, 6.52; N, 9.67; mp: 68.53°C; IR (KBr cm^{-1}) 3247 m, 1738 s, 1612 s, 1504 s, 1469 s, 1423 m, 1307 m, 848 s, 813 w; UV-VIS nm (ε dm^3 mol^{-1} cm^{-1}) 274(44300), 357(28100); ^{1}H NMR (300 MHz, $CDCl_3$): 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).

3-(4′-(4″-Imino(4‴-(n-decyloxy)phenyl)phenyl)-carboxylatophenyl)-1-phenyltriazene-1-oxide, [1d]

Yield: 73%. Anal. Calcd for $C_{36}H_{40}N_4O_4$: C, 72.97; H, 6.76; N, 9.46; found: C, 72.93; H, 6.72; N, 9.49; mp: 79.04°C; IR (KBr cm^{-1}) 3247 m, 1740 s, 1605 s, 1504 s, 1473 s, 1423 m, 1315 m, 837 s, 813 w; UV-VIS nm (ε dm^3 mol^{-1} cm^{-1}) 273(92500), 355(14500); ^{1}H NMR (300 MHz,

$CDCl_3$): 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).

3-(4′-(4″-Imino(4‴-(n-undecyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide, [1e]

Yield: 82%. Anal. Calcd for $C_{37}H_{42}N_4O_4$: C, 73.27; H, 6.93; N, 9.24; found: C, 73.34; H, 6.97; N, 9.27; mp: 85.07°C; IR (KBr cm^{-1}) 3247 m, 1740 s, 1605 s, 1504 s, 1473 s, 1423 m, 1315 m, 837 s, 813 w; UV-VIS nm (ε $dm^3 mol^{-1} cm^{-1}$) 272(58100), 355(38700); ^1H NMR (300 MHz, $CDCl_3$): 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), 8.12 (m, 3H).

3-(4′-(4″-Imino(4‴-(n-dodecyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide, [1f]

Yield: 65%. Anal. Calcd for $C_{38}H_{44}N_4O_4$: C, 72.55; H, 7.09; N, 9.03; found: C, 72.55; H, 7.06; N, 9.07; mp: 85.79°C; IR (KBr cm^{-1}) 3201 m, 1732 s, 1605 s, 1504 s, 1474 s, 1423 m, 1307 m, 837 s, 813 w; UV-VIS nm (ε $dm^3 mol^{-1} cm^{-1}$) 272(23000), 356(24000); ^1H NMR (300 MHz, $CDCl_3$): 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).

3-(4′-(4″-Imino(4‴-(n-tridecyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide, [1g]

Yield: 71%. Anal. Calcd for $C_{39}H_{46}N_4O_4$: C, 73.82; H, 7.25; N, 8.83; found: C, 73.85; H, 7.23; N, 8.81; mp: 95.35°C; IR (KBr cm^{-1}) 3247 m, 1740 s, 1612 s, 1504 s, 1477 s, 1423 m, 1307 m, 837 s, 813 w; UV-VIS nm (ε $dm^3 mol^{-1} cm^{-1}$) 275(28500), 357(43600); ^1H NMR (300 MHz, $CDCl_3$): 0.87 (t, 3H), 1.27 (m, 20H), 1.80 (m, 2H), 3.98 (t, 2H), 6.94 (d, 2H), 7.26 (d, 4H), 8.50 (s, 1H), 7.53 (d, 2H), 7.24 (d, 2H), 7.98 (d, 2H), 7.52 (m, 3H), 10.93 (s, 1H), 8.24 (d, 2H), 8.12 (m, 3H).

3-(4′-(4″-Imino(4‴-(n-tetradecyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide, [1h]

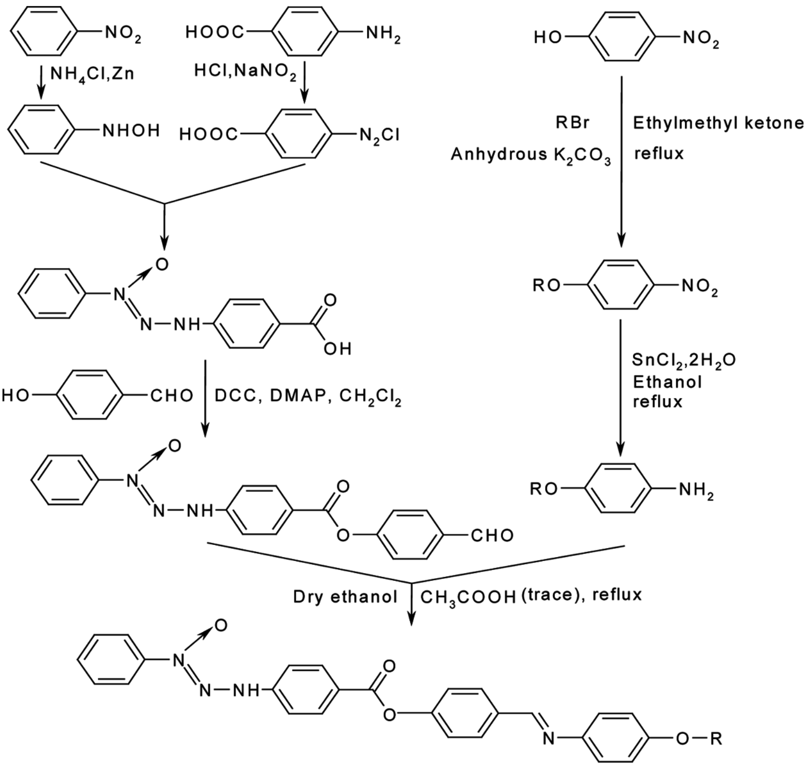
Yield: 68%. Anal. Calcd for $C_{40}H_{48}N_4O_4$: C, 74.07; H, 7.41; N, 8.64; found: C, 74.13; H, 7.43; N, 8.67; mp: 91.82°C; IR (KBr cm^{-1}) 3247 m, 1739 s, 1612 s, 1504 s, 1477 s, 1423 m, 1319 m, 844 s, 813 w; UV-VIS nm (ε dm^3 mol^{-1} cm^{-1}) 275(16300), 356(35500); ^1H NMR (300 MHz, $CDCl_3$): 0.87 (t, 3H), 1.27 (m, 22H), 1.80 (m, 2H), 3.98 (t, 2H), 6.94 (d, 2H), 7.26 (d, 4H), 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).

RESULTS AND DISCUSSION

Synthesis

The 3-(4′-carboxylatophenyl)-1-phenyltriazene-1-oxide has been synthesized by coupling 4-carboxylatophenyldiazonium chloride with β-phenylhydroxylamine following a procedure reported by Sogani and Bhattacharya [2].

The carboxylic acid function of 3-(4′-carboxylatophenyl)-1-phenyltriazene-1-oxide was esterified with *p*-hydroxybenzaldehyde using dicyclohexylcarbodiimide (DCC) and catalytic amount of N,N-dimethylamino-pyridine (DMAP) following a reported method [20]. The final step involves the condensation [22] between 3-(4′-(4″-formylphenyl)-carboxylatophenyl)-1-phenyltriazene-1-oxide and *p*-(n-alkyloxy)aniline to yield the desired product (**1**) as shown in Scheme 1.



(1)

SCHEME 1 Synthesis of 3-(4′(4″-imino(4‴-(n-alkyloxy)phenyl)phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide.

Spectral Properties

The IR spectra of all the compounds show absorptions in the range of 3212–3247 cm^{-1} which are assigned to the N-H stretching vibrations. The lowering in stretching frequency compared to the normal ν_{N-H} stretching vibration indicates the presence of intramolecular hydrogen bonding [23]. Strong absorptions in the region of 1731–1740 cm^{-1} and 1604–1612 cm^{-1} for all the compounds are observed due to the presence of ester [24] and imine [20,24,25] groups, respectively. The ν–N=N–NH– (symmetric triazene) has been found as a multiple band in the range of 1423–1504 cm^{-1} [26]. The $\nu_{N\rightarrow O}$ stretch is observed as a medium band in the region of 1307–1319 cm^{-1} [27]. The $\delta_{N\rightarrow O}$ (bending vibration) has been observed as split bands around 837 cm^{-1} and 813 cm^{-1} [5]. The IR spectrum of representative compound has been shown in Fig. 1.

The electronic spectra of all the compounds in dichloromethane were measured in the region 250–500 nm. All the compounds show two absorption bands, one near 274 nm and the other near 356 nm. The absorption near 356 nm is believed to be $n \rightarrow \pi^*$ transition based on the triazene group [2,28]. The electronic spectrum of representative compound has been shown in Fig. 2.

The low field ^1H NMR signal ~10.9 δ corresponds to the intensity representing the N–H proton [29]. It is observed that the chemical shift of N–H proton remains unaffected by dilution, which indicates the existence of intramolecular hydrogen bonding of the molecules in solution. The signal for aldimine proton uniformly appears at ~8.5

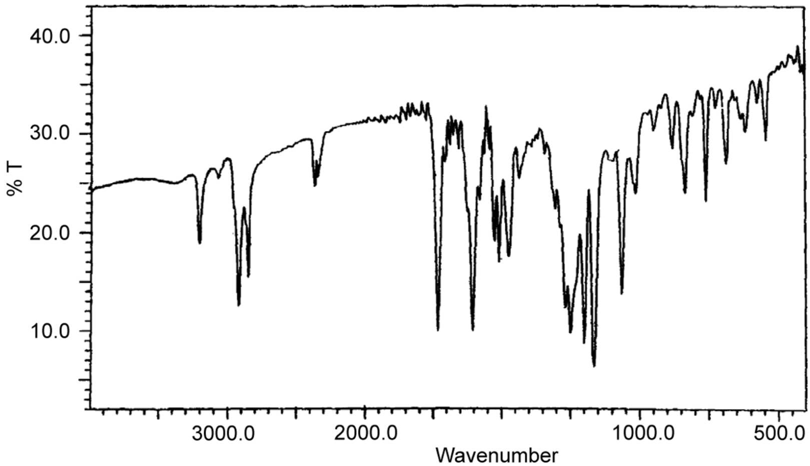


FIGURE 1 Infrared spectrum of **1f** in KBr disc.

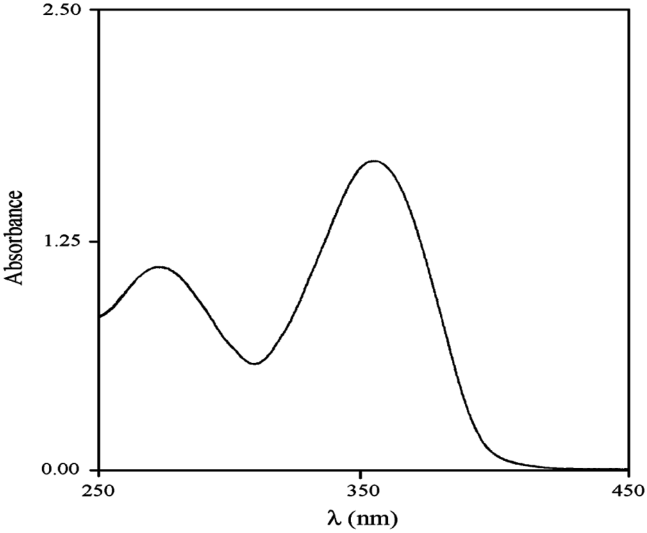


FIGURE 2 Electronic spectrum of **1g** in dichloromethane.

δ [24] for all the members. The specific assignments of the signals for aliphatic and aromatic hydrogen atoms have been made and the chemical shift values (δ, ppm) given in the experimental section, which are in good agreement with the reported chemical shift values of hydrogen atoms in similar environment in the other compounds [30,31]. The ^{1}H NMR spectrum of representative compound has been shown in Fig. 3.

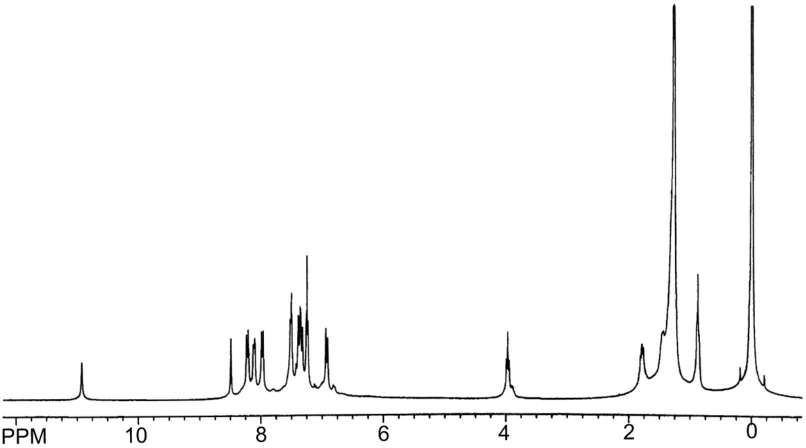


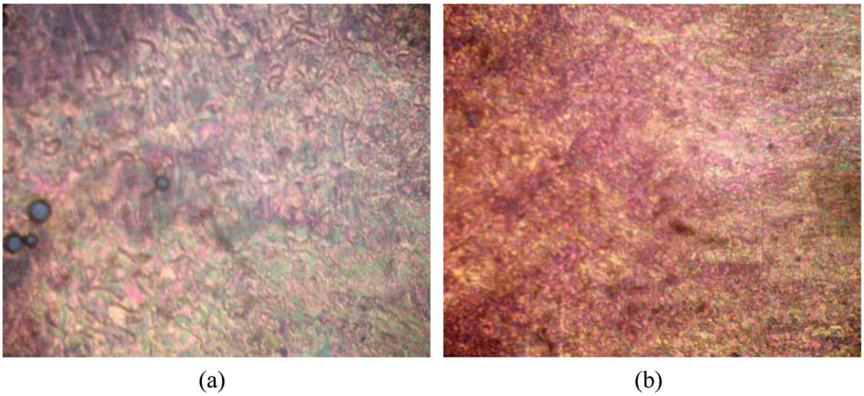
FIGURE 3 ^{1}H NMR spectrum of **1g** in $CDCl_3$.

TABLE 1 Transition Temperatures (°C) Obtained from Optical Microscopic Study for **1a** to **1h**

Comp.	R	Cr	Heating °C Cooling °C	N	Heating °C Cooling °C	I
1a	C_7H_{15}	●	68.5	●	161.0	●
		●	58.4	●	156.7	●
1b	C_8H_{17}	●	70.3	●	175.7	●
		●	52.4	●	160.4	●
1c	C_9H_{19}	●	78.3	●	143.9	●
		●	54.6	●	142.1	●
1d	$C_{10}H_{21}$	●	79.0	●	187.5	●
		●	47.3	●	175.9	●
1e	$C_{11}H_{23}$	●	85.1	●	177.9	●
		●	58.6	●	174.7	●
1f	$C_{12}H_{25}$	●	85.8	●	176.3	●
		●	59.7	●	176.2	●
1g	$C_{13}H_{27}$	●	95.4	●	163.5	●
		●	76.4	●	162.3	●
1h	$C_{14}H_{29}$	●	91.8	●	174.3	●
		●	69.8	●	173.3	●

Thermal Behavior

The transition temperatures for compounds **1a** to **1h** obtained from the optical microscopic studies have been given in the Table 1. All the members show mesomorphic behavior with nematic phase [32] during



(a) (b)

FIGURE 4 Optical texture of compound **1a** at (a) 132°C and (b) 65°C during cooling.

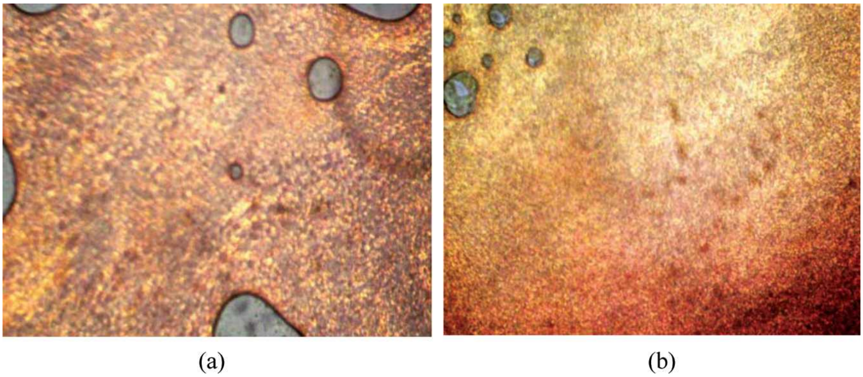

(a) (b)

FIGURE 5 Optical texture of compound **1h** at (a) 125°C and (b) 85°C during cooling.

heating as well as during cooling. Representative optical textures have been shown in Figs. 4 and 5.

The variation of melting point and nematic-isotropic trantransition temperature with the number of carbon atoms (n) in the alkoxy chains of compound (**1**) is shown in Fig. 6. An odd–even effect on transition temperature has been observed for the transition temperatures during

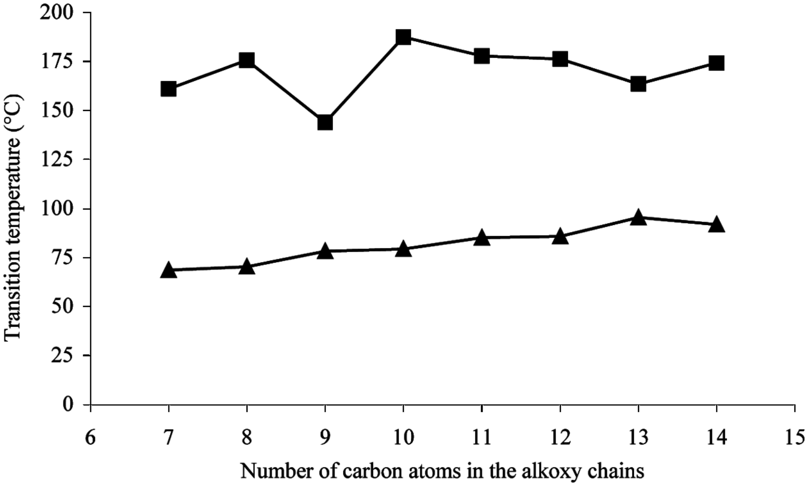


FIGURE 6 Variation of transition temperatures with the number of carbon atoms present in the alkoxy chain during heating. ['—▲—'⇒ solid–nematic, '—■—'⇒ nematic–isotropic transitions.]

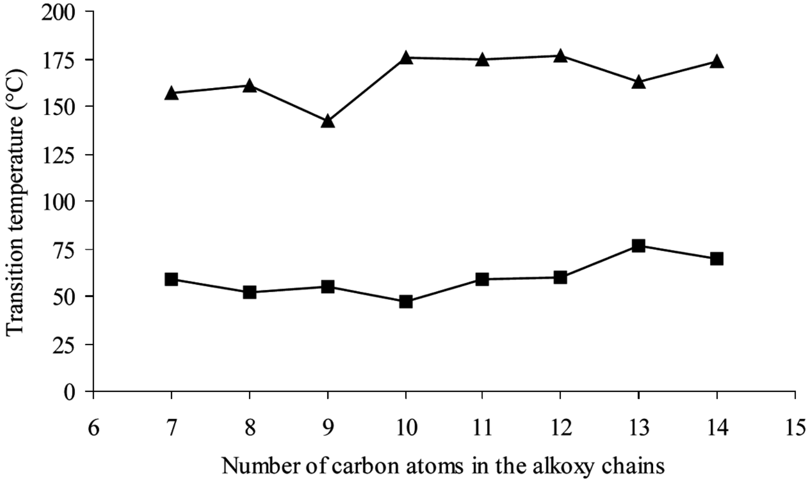


FIGURE 7 Variation of transition temperatures with the number of carbon atoms present in the alkoxy chain during cooling. ['—▲—'⇒ isotropic-nematic, '—■—'⇒ nematic–solid transitions].

heating as well as cooling process. The melting point for any odd member is higher than any even neighbours. The reverse is observed for the clearing temperature Fig. 6.

During cooling the phase entering temperature for any even member is higher than the odd neighbours and the solidification temperature for the odd members are greater than the even neighbours Fig. 7. On cooling the members show the similar pattern of variation of phase transition temperature with the number of carbon atoms (n) of alkoxy chains as that of heating Figs. 6 and 7.

CONCLUSIONS

In our endeavor to incorporate mesogenic behaviour in 1-phenyl-3-phenyltriazene-1-oxide systems, a new series of compounds, 3-(4′-(4″-imino(4‴-(n-alkoxy)phenyl)phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide (**1**) has been designed and successfully synthesized. All the compounds exhibit thermotropic liquid crystalline behaviour over wide range of temperature. All the compounds exhibit nematic phase on melting up to the clearing point during heating as well as on phase entering up to the solidification temperature during cooling. The thermal behavior of metal complexes with this new group of triazene-1-oxides is under investigation.

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