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Liquid Crystals

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Liquid crystalline aryltriazeno-1-oxides with two ester units: synthesis, characterisation, structure and thermal properties

Purak Das^a, Achintesh Narayan Biswas^a, Suvra Acharya^a, Amitava Choudhury^a, Pinaki Bandyopadhyay^{a*} and Pradip Kumar Mandal^b

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A new series of mesogenic triazeno-1-oxides, $C_6H_5-N(O)=N-NH-C_6H_4-C(O)-O-C_6H_4-O-(O)C-C_6H_4-OR$ (**1**, $R=n$ -alkyl group from CH_3 to $C_{14}H_{29}$), was designed and synthesised. All members of this new series were characterised on the basis of spectral and analytical data. The thermotropic liquid crystalline behaviour of the compounds was observed over a wide temperature range using optical microscopy. The mesophase structure was confirmed by a small-angle X-ray diffraction study of a representative member (**1k**). The molecular structure of compound **1i** was determined using the single crystal X-ray diffraction method as a representative case. Dimer formation in the solid state occurs due to intermolecular $N-H...O$ and $C-H...O$ interactions. Intermolecular $C-H...π$ interactions were also detected in **1i**. The intermolecular hydrogen bonding and intermolecular $C-H...π$ interactions arrange the phenyl triazeno-1-oxide fragments of the molecules in layers within the molecular assembly.

1. Introduction

Aryldiazeno-1-oxide derivatives or azoxybenzenes belong to one of the earliest known group of liquid crystalline compounds and have been extensively studied (1). The use of azoxybenzenes in new applications is undergoing a revival as a result of their nonlinear optical and photoisomerisation properties (2). The metallomesogens of azo- and azoxybenzene derivatives constitute another area of current interest for different technological applications (3). Although the liquid crystalline behaviour of aryltriazeno-1-oxide derivatives is well known, the mesogenic behaviour of aryltriazeno-1-oxides or their derivatives has yet to be reported in the literature. However, aryltriazeno-1-oxides and their substituted derivatives are known for their excellent metal binding properties (4), biological relevance (5) and wide applications in analytical chemistry (6). It is well known in the field of liquid crystals that a proper molecular design can enable a targeted mesophase to be achieved. We considered it of interest to investigate some structural modifications of aryltriazeno-1-oxide that would allow the appearance of mesomorphic behaviour. Our design is based on introduction of a flexible rod-like fragment at the 4'-position of aryltriazeno-1-oxide. The fragment consists of two p,p' -substituted phenyl rings as core groups linked via two ester groups. It is known that incorporation of an ester group as linkage between phenyl rings increases the flexibility of the molecular core (7). In this paper, the synthesis, structure and

liquid crystalline behaviour are reported of a new homologous series of compounds (**1**, Scheme 1) derived from aryltriazeno-1-oxide.

2. Experimental section

Preparation of compounds

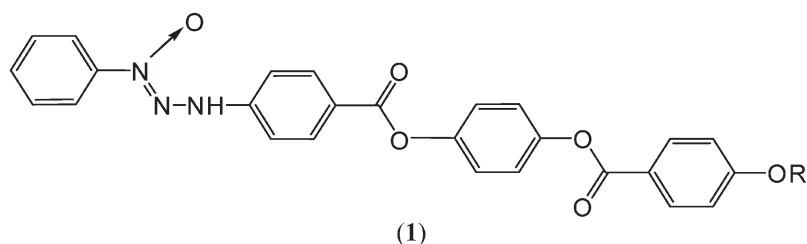
Synthesis of 3-(4'-carboxylatophenyl)-1-phenyltriazeno-1-oxide (I).

3-(4'-Carboxylatophenyl)-1-phenyltriazeno-1-oxide was prepared following a reported method (8). The compound was recrystallised from a mixture of ethanol and acetone (1:1 v/v). Yield: 48%.

Synthesis of 3-(4'-(4''-hydroxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide (II).

A mixture of 3-(4'-carboxylatophenyl)-1-phenyltriazeno-1-oxide (1.03 g, 4 mmol), hydroquinone (0.66 g, 6 mmol), dicyclohexyl carbodiimide (DCC) (0.83 g, 4 mmol) and dimethylaminopyridine (DMAP, 0.05 g, 0.4 mmol) in 1:1.5:1:0.1 molar ratio in dichloromethane (25 ml) was stirred at room temperature for 24 h. The reaction mixture was filtered and the filtrate was collected. Evaporation of solvent produced a mixture of compounds. The 3-(4'-(4''-hydroxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide was isolated by chromatography on silica gel column using a mixture of ethyl acetate and benzene (2:3 v/v) as eluent. Yield: 0.67 g, *ca.* 48%.

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Scheme 1. Structure of the new homologous series derived from aryltriazeno-1-oxide.

Synthesis of 4-(*n*-alkoxy)benzoic acids (**III**).

All the 4-(*n*-alkoxy)benzoic acids were synthesised following a reported procedure (9).

Synthesis of 3-(4'-(4''-octyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide (**1h**).

A mixture of 3-(4'-(4''-hydroxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide (0.35 g, 1 mmol), 4-octyloxybenzoic acid (0.25 g, 1 mmol), DCC (0.21 g, 1 mmol) and DMAP (0.012 g, 0.1 mmol) in 25 ml dichloromethane was stirred for 18 h at room temperature. The mixture was filtered and the filtrate was collected. Removal of solvent afforded a mixture of solid compounds. The resulting mixture was separated using chromatography in a silica gel column and the band eluted by benzene (containing 2% ethyl acetate) was collected. Finally, the compound 3-(4'-(4''-octyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide was crystallised from a mixture of dichloromethane and ethanol (1:4 v/v). Yield: 0.15 g, ca. 25%. ¹H NMR (300 MHz, CDCl₃): 0.90 (t, 3H, H^a), 1.32 (m, 10H, H^b), 1.84 (m, 2H, H^c), 4.06 (t, 2H, H^d), 6.99 (d, 2H, H^e), 8.15 (d, 4H, H^f), 7.28 (d, 4H, H^g), 7.39 (d, 2H, H^h), 10.92 (s, 1H, Hⁱ, N-H), 8.24 (d, 2H, H^j), 7.55 (m, 3H, H^k). IR (KBr, cm⁻¹): ν_{N-H} (3202m), ν_{C=O} (1728s), ν_{N=N-NH-} (1514s, 1478m, 1431m), ν_{N-O} (1302w), δ_{N-O} (847m, 798w). UV-visible: 265 nm (ε = 26 900 dm³ mol⁻¹ cm⁻¹), 357 nm (ε = 40 400 dm³ mol⁻¹ cm⁻¹).

The other compounds of this series were obtained using same procedure as that for 3-(4'-(4''-octyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide. The characterisation data for **1a** and **1n** of this homologous series are summarised below.

For 3-(4'-(4''-methoxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide (**1a**), yield 23.2%. ¹H NMR (300 MHz, CDCl₃): 3.90 (s, 3H, H^d), 6.98 (d, 2H, H^e), 8.15 (d, 4H, H^f), 7.28 (d, 4H, H^g), 7.39 (d, 2H, H^h), 10.93 (s, 1H, Hⁱ, N-H), 8.24 (d, 2H, H^j), 7.51 (m, 3H, H^k). IR (KBr, cm⁻¹): ν_{N-H} (3213m), ν_{C=O} (1739s), ν_{N=N-NH-} (1504s, 1477m, 1423m), ν_{N-O} (1319w), δ_{N-O} (848m, 798w). UV-visible:

264 nm (ε = 27 600 dm³ mol⁻¹ cm⁻¹), 357 nm (ε = 34 500 dm³ mol⁻¹ cm⁻¹).

For 3-(4'-(4''-tetradecyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazeno-1-oxide (**1n**), yield 20.4%. ¹H NMR (300 MHz, CDCl₃): 0.88 (t, 3H, H^a), 1.27 (m, 22H, H^b), 1.83 (m, 2H, H^c), 4.05 (t, 2H, H^d), 6.99 (d, 2H, H^e), 8.14 (d, 4H, H^f), 7.27 (d, 4H, H^g), 7.39 (d, 2H, H^h), 10.92 (s, 1H, Hⁱ, N-H), 8.22 (d, 2H, H^j), 7.52 (m, 3H, H^k). IR (KBr, cm⁻¹): ν_{N-H} (3204m), ν_{C=O} (1726s), ν_{N=N-NH-} (1514s, 1472m, 1433m), ν_{N-O} (1302w), δ_{N-O} (849m, 793w). UV-visible: 265 nm (ε = 26 000 dm³ mol⁻¹ cm⁻¹), 358 nm (ε = 38 400 dm³ mol⁻¹ cm⁻¹).

Characterisation

General.

Infrared spectra were recorded using a JASCO 5300 FT-IR spectrometer. Electronic spectra were obtained using a Perkin-Elmer Lambda 2S spectrophotometer. ¹H NMR spectra were recorded on a Bruker DPX 300 spectrometer. Microanalyses (C, H, N) were performed using an Elementar Vario EL III Carlo Erba 1108 elemental analyser.

Mesophase.

Optical microscopic studies at different temperatures were performed using a polarising microscope (Manufacturer: Labex K.K. International, India; Model: Co ax 10B(POL), 150X). The probe temperature was controlled using a Mettler FP 80 control system and FP82 hot stage. The setup for small-angle X-ray diffraction has been reported previously (10). Small-angle X-ray photographs were taken at room temperature and within the mesomorphic range using Nickel-filtered Cu K_α radiation; the temperature was regulated within ±0.5°C by a controller (Indotherm 401-D2, India).

Structure

A suitable crystal of **1i** was mounted on a glass fibre and transferred to a Bruker SMART CCD single-crystal diffractometer. At room temperature,

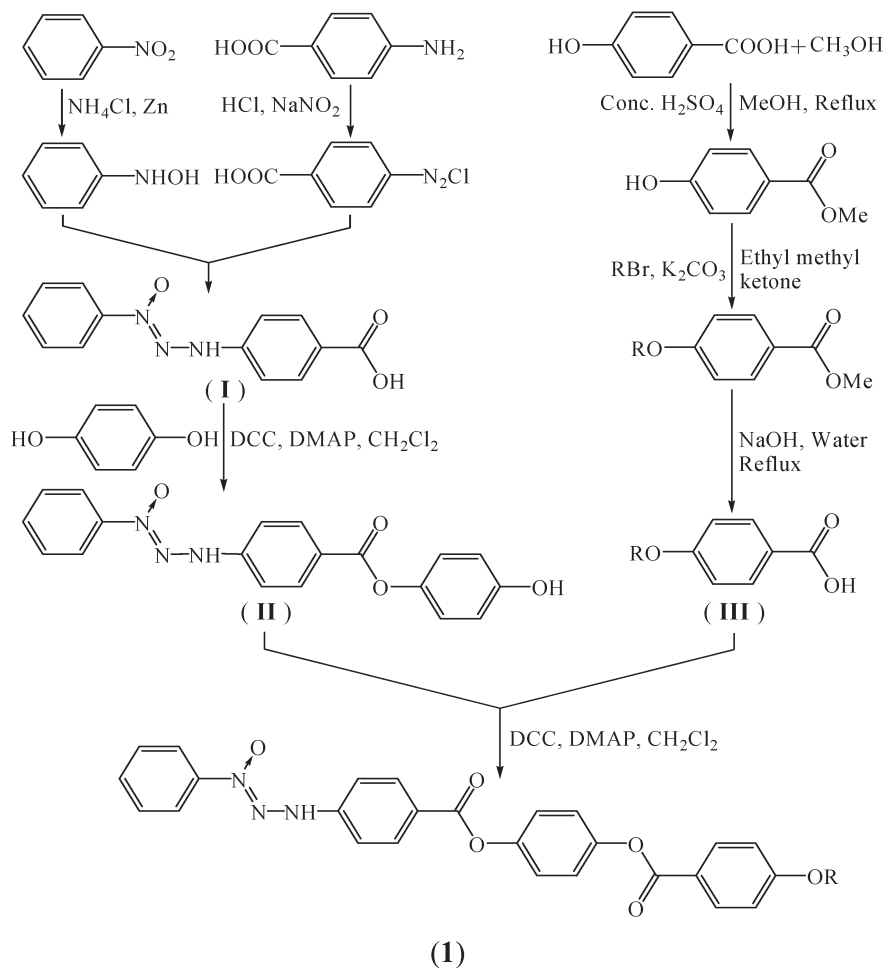
three-dimensional X-ray data were collected by the ω scan method using graphite-monochromated Mo K α radiation. The structure was solved by direct methods using SHELXS-97 and difference Fourier syntheses. All the hydrogen positions were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out. Data collection and refinement were performed using the following packages: data collection, *SMART* (11); cell refinement, *SAINTE* (12); data reduction, *SAINTE*; absorption correction, *SADABS* (13); programs used to solve structure, *SHELXS97* (14); programs used to refine structure, *SHELXL97* (14); molecular graphics, *SHELXTL* (15).

3. Results and discussion

Synthesis

The synthesis of 3-(4'-(4''-alkyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazene-1-oxides (**1**) involves multiple steps. The synthetic route is depicted in the Scheme 2. Initially the 3-(4'-carboxylatophenyl)-1-phenyltriazene-1-oxide (**I**) was synthesised following a reported method (8) and the carboxylic group of 3-(4'-carboxylatophenyl)-1-phenyltriazene-1-oxide (**I**) was esterified with hydroquinone (16) to yield 3-(4'-(4''-hydroxyphenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide (**II**).

The final product, 3-(4'-(4''-alkyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazene-1-oxides (**1**), was obtained by esterification of 3-(4'-(4''-hydroxyphenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide (**II**) with 4-(*n*-alkyloxy)benzoic acid (**III**). The elemental analysis data of the compounds are shown in Table 1.



Scheme 2. Synthesis of 3-(4'-(4''-alkyloxybenzoyloxyphenyl)carboxylatophenyl)-1-phenyltriazene-1-oxides (**1**).

Table 1. Microanalysis data for compounds **1a–1n**.

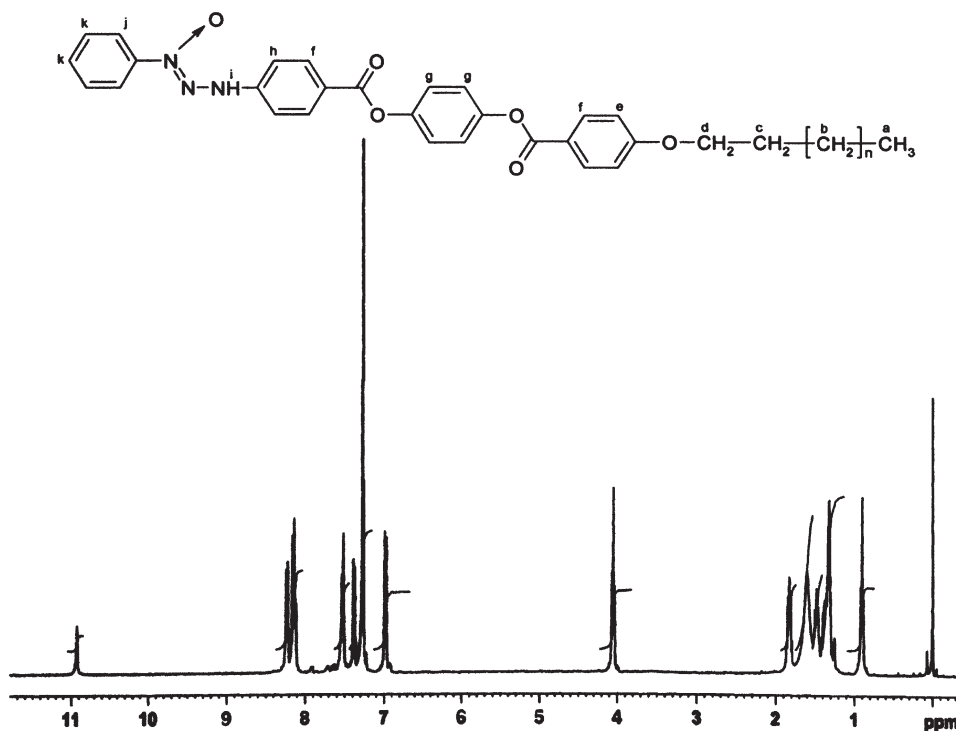
Compound	R	Carbon %		Hydrogen %		Nitrogen %	
		Calculated	Found	Calculated	Found	Calculated	Found
1a	CH ₃	67.08	67.14	4.35	4.31	8.70	8.63
1b	C ₂ H ₅	67.61	67.58	4.63	4.59	8.45	8.40
1c	C ₃ H ₇	68.10	68.16	4.89	4.91	8.22	8.17
1d	C ₄ H ₉	68.57	68.54	5.14	5.17	8.00	8.07
1e	C ₅ H ₁₁	69.02	69.09	5.38	5.36	7.79	7.83
1f	C ₆ H ₁₃	69.44	69.47	5.61	5.57	7.59	7.54
1g	C ₇ H ₁₅	69.84	69.74	5.82	5.87	7.41	7.37
1h	C ₈ H ₁₇	70.22	70.19	6.02	6.07	7.23	7.27
1i	C ₉ H ₁₉	70.59	70.60	6.22	6.24	7.06	6.99
1j	C ₁₀ H ₂₁	70.94	70.99	6.40	6.37	6.89	6.87
1k	C ₁₁ H ₂₃	71.27	71.31	6.58	6.51	6.74	6.79
1l	C ₁₂ H ₂₅	71.58	71.49	6.75	6.69	6.59	6.63
1m	C ₁₃ H ₂₇	71.89	71.83	6.91	6.97	6.45	6.38
1n	C ₁₄ H ₂₉	72.18	72.09	7.07	6.96	6.32	6.31

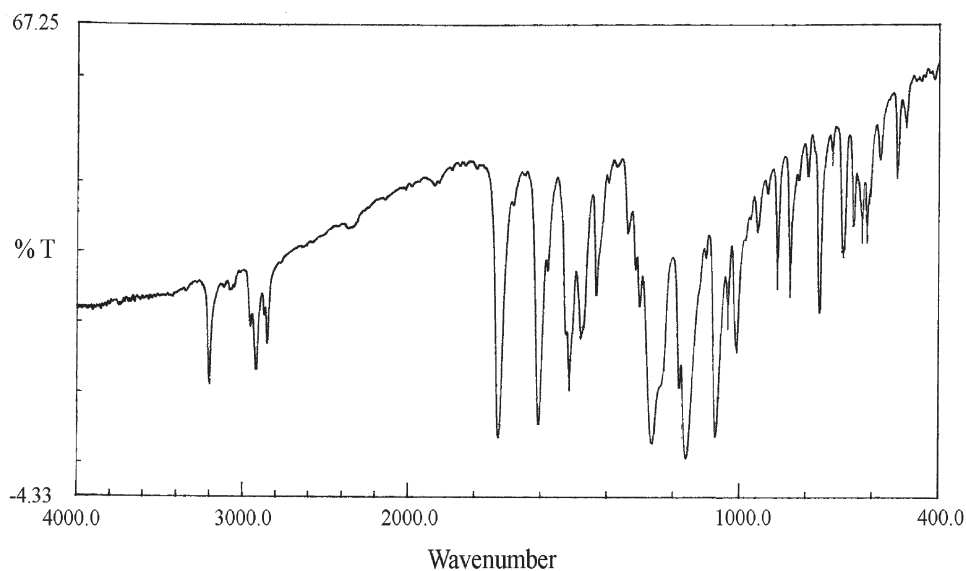
Spectral properties

As an example, the ¹H NMR spectrum of **1g** is shown in Figure 1. The ¹H NMR signal for N–H proton uniformly appears at ~10.9δ (17). The specific assignments of the signals for aliphatic and aromatic hydrogen atoms have been made (18) and the corresponding proton signals are presented in the experimental section.

Also as an example, the IR spectrum of **1i** is shown in Figure 2. The IR spectra of all the compounds show absorptions in the range 3212–3247 cm⁻¹, which are

assigned to the N–H stretching vibration. The lowering in stretching frequency compared to the normal ν_{N–H} stretching vibration indicates the presence of an intramolecular hydrogen bonding (19). Strong absorptions in the region 1731–1740 cm⁻¹ for all the compounds are observed due to the presence of an ester group (20). The ν_{N=N–NH} (symmetric triazene) vibration is observed as a multiple band in the range 1423–1504 cm⁻¹ (21). The ν_{N→O} stretch is observed as a medium band in the region 1307–1319 cm⁻¹ (22). The δ_{N→O} (bending

Figure 1. ¹H NMR spectrum of **1g**.

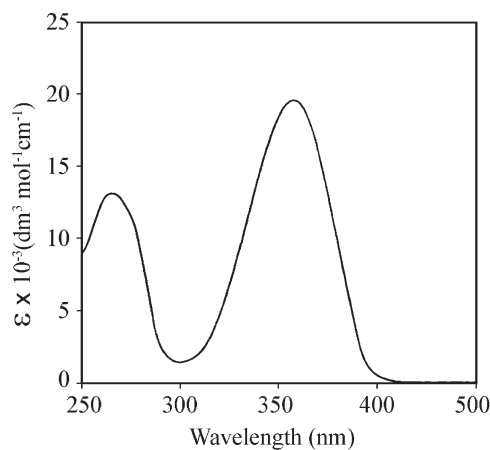
Figure 2. IR spectrum of **1i**.

vibration) is observed as split bands around 837 cm^{-1} and 813 cm^{-1} (23).

The electronic spectrum of compound **1h** is shown in Figure 3 as an example. The electronic spectra of all the compounds in dichloromethane were measured in the region 250–450 nm. All the compounds uniformly show two absorptions near 264 and 358 nm. The absorption at about 358 nm is assigned as a $\pi \rightarrow \pi^*$ transition (24).

Liquid crystalline behaviour

The liquid crystalline behaviour of all the compounds of the series (**1a–1n**) was studied using polarising optical microscopy. The presence of a mesophase was confirmed by the small-angle X-ray diffraction study of **1k** as a representative member of the series.

Figure 3. Electronic spectrum of **1h** in dichloromethane.

Optical microscopy.

The different transition temperatures recorded from the optical microscopic study are recorded in Table 2.

Table 2. Transition temperatures ($^{\circ}\text{C}$) obtained from optical microscopic study of **1a–1n**.

Compound	Heating / $^{\circ}\text{C}$		Heating / $^{\circ}\text{C}$		Heating / $^{\circ}\text{C}$	
	Cr ₁	Cooling / $^{\circ}\text{C}$	Cr ₂	Cooling / $^{\circ}\text{C}$	N	Cooling / $^{\circ}\text{C}$
1a	• 109.5	–	•	239.5	•	•
	• 92.5	–	•	238.3	•	•
1b	• 110.5	–	•	234.5	•	•
	• 85.8	–	•	231.3	•	•
1c	• 102.5	–	•	195.6	•	•
	• 98.7	–	•	193.2	•	•
1d	• 105.6	–	•	240.4	•	•
	• 99.8	–	•	236.4	•	•
1e	• 44.9	–	•	192.7	•	•
	• 42.8	–	•	185.2	•	•
1f	• 67.7	–	•	182.4	•	•
	• 41.1	–	•	177.4	•	•
1g	• 43.5	–	•	165.4	•	•
	• 38.7	–	•	159.3	•	•
1h	• 47.9	–	•	185.5	•	•
	• 36.3	–	•	182.8	•	•
1i	• 49.5	• 61.4	•	196.5	•	•
	• 38.3	–	•	195.6	•	•
1j	• 42.4	• 62.7	•	168.7	•	•
	• 35.8	–	•	163.3	•	•
1k	• 40.4	• 68.6	•	158.9	•	•
	• 38.6	–	•	154.3	•	•
1l	• 57.1	• 71.1	•	156.5	•	•
	• 41.8	–	•	151.4	•	•
1m	• 45.0	• 73.8	•	142.4	•	•
	• 42.7	–	•	130.5	•	•
1n	• 55.6	• 66.3	•	149.6	•	•
	• 43.0	–	•	146.8	•	•

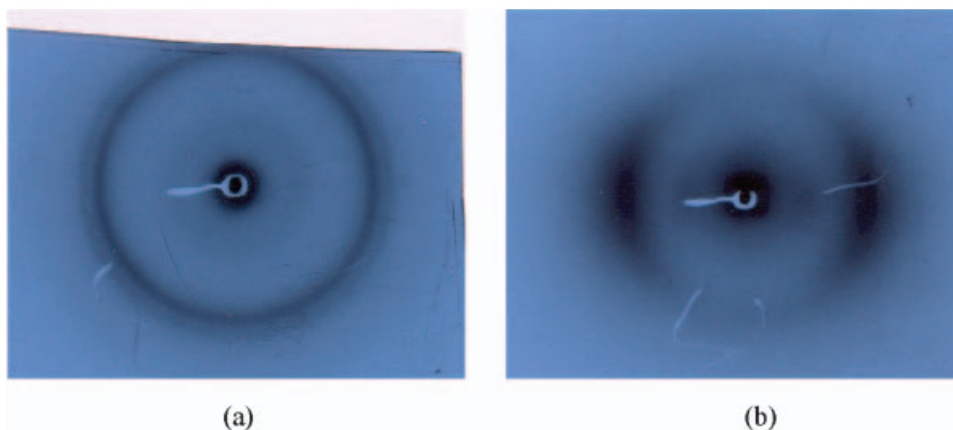


Figure 4. X-ray diffraction photograph of **1k** at (a) room temperature in the solid state and (b) 75°C in the nematic phase.

All the compounds exhibit only a nematic phase (25) on melting from the crystalline state. Higher members of this homologous series (**1i–1n**) exhibit a solid–solid transition at lower temperatures during heating. On cooling, all the compounds of the series exhibit only a nematic phase, which continues down to the solidification temperature (Table 2).

The sensitivity of the compounds towards light was also examined. Each compound was kept above the nematic (N)–isotropic (I) transition temperature for 30 min with maximum possible illumination. No change was observed. Subsequently, both the I–N and N–I transition temperatures were recorded and showed no variation from those determined without long exposure to light. Thus, compounds **1a–1n** are stable to the exposure of light.

Small-angle X-ray diffraction.

A small-angle X-ray diffraction analysis was performed to confirm the existence of a mesophase in the above series of compounds. Small-angle X-ray diffraction photographs of a representative member of the series, i.e. **1k**, were taken at room temperature and also for magnetically aligned **1k** at 75°C. The resulting X-ray diffraction photographs of **1k** at room temperature and in the mesogenic phase are shown in Figure 4. The small angle X-ray diffraction

study for the compound confirms the existence of a mesophase in the present series of compounds. An analysis of the X-ray diffraction photograph of **1k** taken in the mesophase infers that the phase present in the compound at 75°C is a cybotactic nematic.

Single crystal X-ray diffraction

The molecular structure of the present series of compounds was confirmed by a single crystal X-ray diffraction study of a representative member (**1i**) of the series at room temperature. The molecular geometry of **1i** with atomic numbering is shown in Figure 5. The calculated length of the **1i** molecule in the crystalline state is found to be 34.83 Å, whereas the model length in the most extended form is 36.35 Å. Thus the molecule is slightly bow-shaped. The crystal data collection parameters are listed in Table 3. The structure of **1i** has been solved along with some disorder at C4, C5, H4 and H5 atoms. This disorder was the result of high thermal parameters of the atoms at room temperature, which resulted in a structure factor in the overall solution.

Selected bond lengths and bond angles are collected in Table 4. The essentially planar phenyl moiety and trigonal planar geometry of the triazene N3 atom strongly suggest a resonance interaction extending over the C1, N1, N2 and N3 atoms (torsion

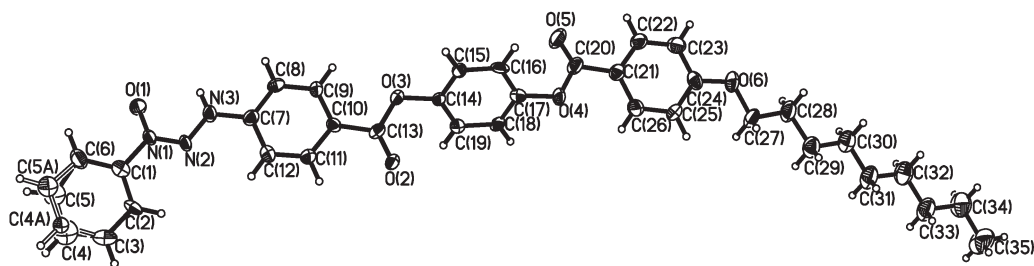


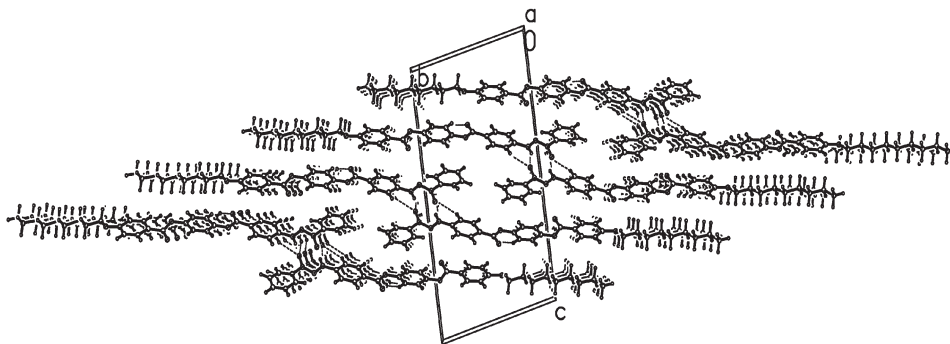
Figure 5. The asymmetric unit of **1i**, with displacement ellipsoids drawn at the 70% probability level.

Table 3. Crystal data and structure refinement for **1i**.

Empirical formula	C ₃₅ H ₃₇ N ₃ O ₆
Formula weight	595.68
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a=5.752(2)$ Å $\alpha=80.676(7)^\circ$ $b=12.189(5)$ Å $\beta=88.531(7)^\circ$ $c=23.057(9)$ Å $\gamma=84.640(7)^\circ$
Volume	1588.0(11) Å ³
Z	2
Density (calculated)	1.246 Mg m ⁻³
Absorption coefficient	0.086 mm ⁻¹
$F(000)$	632
Crystal size	0.25 × 0.04 × 0.02 mm ³
Theta range for data collection	1.79 to 25.00°
Index ranges	$-6 \leq h \leq 6$, $-14 \leq k \leq 14$, $-27 \leq l \leq 27$
Reflections collected	13 871
Independent reflections	5220 [$R(\text{int})=0.0596$]
Completeness to theta=25.00°	93.5%
Absorption correction	Empirical
Max. and min. transmission	0.998000 and 0.979000
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5220/12/394
Goodness-of-fit on F^2	1.321
Final R indices [$I > 2\sigma(I)$]	$R1=0.1507$, $wR2=0.2261$
R indices (all data)	$R1=0.2041$, $wR2=0.2465$
Largest diff. peak and hole	0.266 and -0.211 e Å ⁻³

Table 4. Selected bond lengths (Å) and bond angles (°) for **1i**.

C(1)–N(1)	1.441(7)	N(1)–O(1)	1.267(5)
N(1)–N(2)	1.268(5)	N(2)–N(3)	1.320(5)
N(3)–C(7)	1.398(7)	N(3)–H(3A)	0.8600
C(6)–C(1)–N(1)	117.8(5)	O(1)–N(1)–N(2)	125.3(4)
O(1)–N(1)–C(1)	120.1(4)	N(2)–N(1)–C(1)	114.6(4)
N(1)–N(2)–N(3)	111.6(4)	N(2)–N(3)–C(7)	118.6(4)
N(2)–N(3)–H(3A)	120.7	C(7)–N(3)–H(3A)	120.7

Figure 6. The molecular packing of **1i** showing the arrangements of the molecules in the ac -plane.

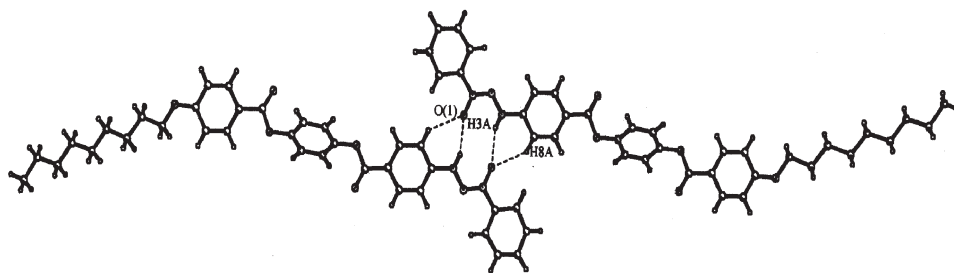
angle=179.87°). The N1–N2 and N2–N3 distances are 1.268(5) Å and 1.320(5) Å, respectively; these observed values agree with the reported values of other triazene-1-oxides (26). The shorter length of N1=N2 indicates its double-bond character and the longer N2–N3 distance [1.320(5) Å] is still shorter than a pure single bond. The deviation of O1 from the molecular plane causes conjugation between N1–C1 to be less effective and is reflected in the longer N1–C1 [1.441(7) Å] than N3–C7 distance [1.398(7) Å]. The almost planar conformation of the triazene fragment of the molecule is a result of intermolecular hydrogen bonding (*vide infra*).

The CO double bonds, C13=O2 and C20=O5, are found to be 1.186(6) Å and 1.183(6) Å, respectively, whereas CO single bonds C13–O3 and C20–O4 are 1.356(6) Å and 1.349(7) Å, respectively. The molecular packing of **1i** showing the arrangements of the molecules in the ac -plane is shown in Figure 6.

Intermolecular hydrogen bonding causes dimer formation of **1i** (Figure 7). The hydrogen bonding involves both N–H and C–H groups with an oxygen atom of triazene-1-oxide. There are two N–H...O interactions and two C–H...O interactions, details of which are given in Table 5. The intermolecular C–H... π interactions involve the centroid of the phenyl ring C21→C26 (Cg2) with the aryl H3B and alkyl H28B hydrogen atoms (Figure 8). The H...Cg distances are 2.76 and 2.79 Å, respectively (Table 5).

The intermolecular hydrogen bonding and intermolecular C–H... π interactions make the phenyltriazene-1-oxide fragments of **1i** form a layer arrangement (Figure 9) in the molecular assembly.

From these figures it is evident that the pairs of molecules related by the centre of inversion are arranged in a parallel manner. These pairs of parallel molecules are packed in interpenetrating layers (Figure 9). The molecular assembly suggests that, on heating, the opposite shift of pairs parallel to each other may give rise to mesophase structure.

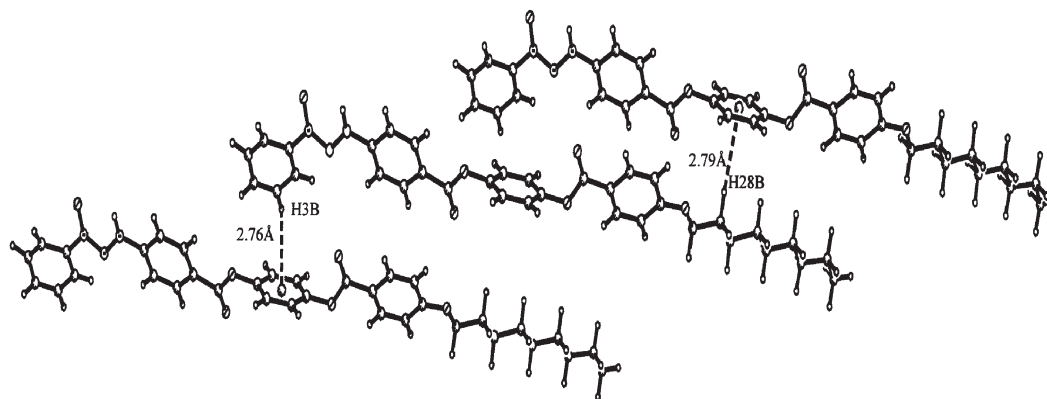
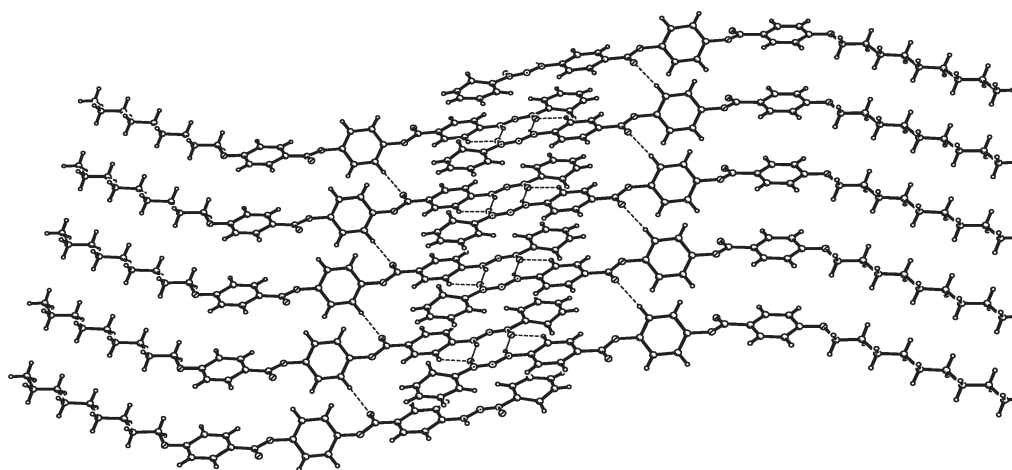
Figure 7. Dimerisation of two molecules of **1i** through intermolecular hydrogen bonding.Table 5. Hydrogen-bonding geometry of **1i**.

D—H \cdots A	D—H/Å	H \cdots A/Å	D \cdots A/Å	D—H \cdots A/ $^{\circ}$
N3—H3A \cdots O1	0.86	2.15	2.493(6)	103
N3—H3A \cdots O1 ⁱ	0.86	2.14	2.941(6)	156
C8—H8A \cdots O1 ⁱ	0.93	2.47	3.237(8)	140
C15—H15A \cdots O2 ⁱⁱ	0.93	2.49	3.372(7)	158
C3—H3B \cdots Cg2 ⁱⁱⁱ	0.93	2.76	3.544(7)	143
C28—H28 \cdots Cg2 ^{iv}	0.97	2.79	3.746(7)	170

Symmetry codes: (i) $2-x, -y, 1-z$; (ii) $1+x, y, z$; (iii) $-1+x, -1+y, z$; (iv) $x, 1+y, z$; Cg2 is the centroid of the phenyl ring C14 \rightarrow C19.

4. Conclusions

Compounds (**1a–1n**) of a new homologous series have been designed, synthesised and characterised. All the members of this family exhibit thermotropic liquid crystalline behaviour over a wide temperature range. All the compounds exhibit a nematic phase on melting. Compounds **1i–1n** exhibit a solid–solid phase transition at lower temperatures during heating. A small-angle X-ray diffraction study of a

Figure 8. The intermolecular C–H \cdots π interactions are shown by the dashed bond.Figure 9. Layer formation through intermolecular hydrogen bonding and intermolecular C–H \cdots π interactions of **1i** in crystalline state.

representative member (**1k**) confirmed the presence of mesophases in the present series of compounds.

The molecular structures of the present series of compounds were investigated by an X-ray diffraction study of a representative member of the series (**1i**). The intermolecular hydrogen bonding causes dimer formation in **1i**. There are both N–H...O and C–H...O interactions. The intermolecular hydrogen bonding and C–H... π interactions hold the phenyl-triazene-1-oxide fragments of **1i** in a layer arrangement within the molecular assembly.

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Supplementary material

Crystallographic data for structural analysis of **1i** have been deposited at the Cambridge Crystallographic Data Centre, CCDC, No. 280242. Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336033, email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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