Liquid Crystals
Publication details, including instructions for authors and subscription information:
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[a] Department of Chemistry, University of North Bengal, Siliguri 734013, India [b] Department of Physics, University of North Bengal, Siliguri 734013, India [c] Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi 110016, India

To cite this Article Das, Purak , Narayan Biswas, Achintesh , Choudhury, Amitava , Bandyopadhyay, Pinaki , Haldar, Sripada , Mandal, Pradip Kumar and Upreti, Shailesh(2008) 'Novel synthetic route to liquid crystalline 4,4'-bis(*n*-alkoxy)azoxybenzenes: spectral characterisation, mesogenic behaviour and crystal structure of two new members', Liquid Crystals, 35: 5, 541 — 548

To link to this Article: DOI: 10.1080/02678290802015705

URL: http://dx.doi.org/10.1080/02678290802015705

Liquid Crystals,
Vol. 35, No. 5, May 2008, 541–548

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Novel synthetic route to liquid crystalline 4,4′-bis(*n*-alkoxy)azoxybenzenes: spectral characterisation, mesogenic behaviour and crystal structure of two new members

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[a]*Department of Chemistry, University of North Bengal, Siliguri 734013, India;* [b]*Department of Physics, University of North Bengal, Siliguri 734013, India;* [c]*Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi 110016, India*

(Received 28 December 2007; final form 26 February 2008)

A simple synthetic method has been developed for the preparation of long-chain 4,4′-bis(*n*-alkoxy)azoxybenzenes by reductive coupling of 4-*n*-alkoxynitrobenzenes using zinc powder and ammonium chloride in aqueous ethanol medium at ambient temperature. The new method was employed to synthesise known members (n=1–12) of the 4,4′-bis(*n*-alkoxy)azoxybenzene ($C_nH_{2n+1}OPhN(O)=NPhOC_nH_{2n+1}$) series and also two hitherto unknown members (n=13–14) of the series. The new compounds were characterised using spectral (IR, UV–visible, ^{1}H NMR and FAB-MS) data. The mesogenic behaviour of both compounds was studied by polarising optical microscopy, differential scanning calorimetry and small-angle X-ray diffraction techniques. The crystal structure of 4,4′-bis(*n*-tetradecyloxy)azoxybenzene was determined using single-crystal X-ray diffraction data. The packing of the molecules in the crystalline state is found to be a precursor to the smectic C phase structure.

Keywords: smectic phase precursor; crystal structure; 4,4′-bis(*n*-alkoxy)azoxybenzenes

1. Introduction

Azoxybenzenes, one of the earliest known group of liquid crystalline compounds (*1–4*), were contemplated as being useful in display devices, but subsequently were found unsuitable due their coloured nature and instability. However, there is a revived interest for their use in new applications, such as those involving nonlinear optical properties and photoisomerisation (*5, 6*). The metallomesogens of azo- and azoxybenzene derivatives is another area of current interest for different technological applications (*7–9*).

The mesogenic behaviour of azoxybenzenes is mainly confined within two groups of compounds, i.e. 4,4′-bis(*n*-alkoxy)azoxybenzenes and 4,4′-bis(*n*-alkyl)azoxybenzenes (*10–18*). Lower homologues (n=1–6) of the 4,4′-bis(*n*-alkoxy)azoxybenzene series ($C_nH_{2n+1}OPhN(O)=NPhOC_nH_{2n+1}$) exhibit only a nematic phase, whereas the mid-members (n=7–10) exhibit both nematic and smectic mesophases. The higher homologues (n=11, 12) exhibit only a smectic phase (*3*). Members with very high *n*-values (n=16 and 18) show two smectic modifications, smectic I (SmI) and smectic C (SmC), on the basis of a miscibility study (*11, 19*). A few members (n=1, 6 and 12) of this series are found to exhibit an induced smectic A (SmA) phase when mixed with bi-swallow-tailed compound having SmC and nematic phases (*20*). Only the seventh member of this series is reported to exhibit an induced ferroelectric SmC phase when dissolved in chiral dopants (*21*).

In this paper, a new single step synthesis is reported of long-chain 4,4′-disubstituted azoxybenzenes by an operationally easy reduction of the corresponding nitroarenes using inexpensive zinc powder and ammonium chloride in aqueous ethanol. The synthesis, spectral characterisation and liquid crystalline behaviour of two hitherto unknown members (n=13–14) of the series are also reported. The knowledge of the molecular geometry and packing of the molecules in the crystalline state often helps in explaining the observed phase behaviour, which depends on a subtle balance of intermolecular interactions (*22, 23*). With this aim, the results of a single-crystal X-ray diffraction study of 4,4′-bis(*n*-tetradecyloxy)azoxybenzene are presented.

2. Experimental

Characterisation

Infrared spectra, electronic spectra and ^{1}H NMR spectra were recorded using a JASCO 5300 FT-IR spectrometer, Perkin-Elmer Lambda 2S spectrophotometer and Bruker DPX 300 spectrometer, respectively. The FAB mass spectra were recorded on a JOEL SX 102/DA-600 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) at CDRI, Lucknow, India. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol was used as the matrix. The matrix peaks appear at *m*/*z* 136, 137, 154, 289, 307 in

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*Corresponding author. Email: pbchem@rediffmail.com

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290802015705
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the absence of any metal ions. Microanalyses (C, H, N) were performed using an Elementan Vario EL III Carlo Erban 1108 elemental analyser.

Preparation of materials

Syntheses of 4,4′-bis(n-alkoxy)azoxybenzenes.

All the compounds of the 4,4′-bis(n-alkoxy)azoxybenzenes series (n=1–14) have been synthesised following same procedure. The yields (isolated in pure form) of all the members of the series are given in Table 1. The synthesis of 4,4′-bis(n-tridecyloxy)azoxybenzene is described below as an example.

*4,4′-bis(n-tridecyloxy)azoxybenzene (**1-13**).*

4-(*n*-Tridecyloxy)nitrobenzene (3.2 g, 10 mmol) was taken in 100 ml of a mixture of ethanol and water (9:1 v/v). The mixture was warmed (333 K) with stirring till the solution became clear. To the above mixture, water (25–40 ml) was added slowly till faint turbidity appeared. To this reaction mixture, ammonium chloride (1.07 g, 20 mmol) was added and heating was stopped. Zinc powder (1.96 g, 30 mmol) was added to the reaction mixture very slowly over 10 min. The reaction mixture was further stirred for 1 h. The resulting reaction mixture was diluted with an equal volume of cold water and then filtered under suction. The yellow residue mixed with zinc oxide was extracted with dichloromethane. After removal of the solvent the yellow solid was collected. This was dissolved in a minimum volume of dichloromethane (~5 ml) and the solution was separated on silica gel using a preparative thin-layer chromatographic (TLC) technique using 2–3% ethyl acetate in petroleum ether (boiling range 60–80°C) as eluant. The preparative TLC plate was found to contain two bands. The first band was yellow in colour and found to contain the 4,4′-bis(*n*-tridecyloxy)azobenzene (**2-13**) (yield: 0.12 g; 4.13%). The following pale yellow band contained 4,4′-bis(*n*-tridecyloxy)azoxybenzene (**1-13**). Yield: 1.58 g, 53.20%. ^{1}H NMR: 0.88 (t, 6H); 1.32 (m, 40H); 1.82 (m, 4H); 4.02 (t, 4H); 6.95 (m, 4H); 8.26 (d, 2H); 8.21 (d, 2H). IR (KBr, cm^{-1}): 1462s (s)ν_{N-O}, 1256s (as)ν_{N-O}. UV–visible: 360 nm (ε=22 800 dm^3 mol^{-1} cm^{-1}). FAB-MS: 596 (Calc. 594). Elemental analysis: calculated for $C_{38}H_{62}N_2O_3$, C 76.77, H 10.44, N 4.71; found C 76.83, H 10.37, N 4.78%.

Table 1. Zinc–ammonium chloride mediated reductive coupling of 4-RO-nitrobenzene to corresponding azoxy- and azobenzenes.

Entry No.	R	Azoxy product	Yield[a] (%)	Azo product	Yield[a] (%)
1	CH_3	**1-1**	44.8	**2-1**	10.1
2	C_2H_5	**1-2**	53.9	**2-2**	13.4
3	C_3H_7	**1-3**	56.3	**2-3**	6.7
4	C_4H_9	**1-4**	52.2	**2-4**	8.1
5	C_5H_{11}	**1-5**	62.6	**2-5**	8.2
6	C_6H_{13}	**1-6**	54.9	**2-6**	6.9
7	C_7H_{15}	**1-7**	60.2	**2-7**	3.7
8[b]	C_8H_{17}	**1-8**	55.0	**2-8**	4.4
9	C_9H_{19}	**1-9**	51.7	**2-9**	3.8
10	$C_{10}H_{21}$	**1-10**	55.2	**2-10**	5.5
11	$C_{11}H_{23}$	**1-11**	56.1	**2-11**	6.5
12	$C_{12}H_{25}$	**1-12**	51.3	**2-12**	3.9
13	$C_{13}H_{27}$	**1-13**	53.2	**2-13**	4.1
14	$C_{14}H_{29}$	**1-14**	50.8	**2-14**	4.0

[a]Isolated in pure form; [b]Ref. (*33*).

*4,4′-bis(n-tetradecyloxy)azoxybenzene (**1-14**).*

The synthetic method is similar to that of 4,4′-bis(*n*-tridecyloxy)azoxybenzene. Here 4,4′-bis(*n*-tetradecyloxy) azoxybenzene (**1-14**) is the major product. Yield: 1.58 g, 50.80%. ^{1}H NMR: 0.88 (t,6H); 1.30 (m, 44H); 1.81 (m, 4H); 4.02 (t, 4H); 6.95 (m, 4H); 8.26 (d, 2H); 8.21 (d, 2H). IR (KBr, cm^{-1}): 1462s (s)ν_{N-O}, 1256s (as)ν_{N-O}. UV–visible: 359 nm (ε =26100 dm^3 mol^{-1} cm^{-1}). FAB-MS: 624 (calculated 622). Elemental analysis: calculated for $C_{40}H_{66}N_2O_3$, C 77.17, H 10.61, N 4.50; found, C 77.14, H 10.62, N 4.56%.

A yellow band of the corresponding azo compound (**2-14**) was collected (yield: 0.12 g, 3.97%).

Liquid crystalline properties

Microscopic studies at different temperatures were performed using a polarising optical microscope (Labex KK International, India; Co ax 10B(POL), 150X). The probe temperature was controlled using Metler FP 80 control system and FP82 hot stage. Differential scanning calorimetric (DSC) measurements were performed using a Mettler thermosystem FP84 or Pyris-6 differential scanning calorimeter with a heating and cooling rate of 3–5°C min^{-1}. The setup used for small-angle X-ray diffraction was reported elsewhere (*24*). Small-angle X-ray photographs were taken throughout 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 determination and refinement

A suitable crystal of **1-14** was mounted on a glass fibre and transferred to a Bruker SMART CCD single-crystal diffractometer. 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. The data collection and refinement were carried out using the following packages. For data collection, *SMART* (*25*); cell refinement and data reduction, *SAINT* (*26*); absorption correction, *SADABS* (*27*); programs used to solve and refine the structure, *SHELXS97* and *SHELXL97* (*28*); molecular graphics, *SHELXTL* (*29*).

3. Results and discussion

Synthesis

The most common synthetic route to prepare the mesogenic symmetrical or unsymmetrical 4,4′-*n*-dialkyl/alkyloxyazoxybenzenes is the oxidation of corresponding 4,4′-*n*-dialkyl/alkyloxyazobenzenes (*30*). Mesogenic symmetrical 4,4′-di-*n*-alkylazoxybenzenes can also be synthesised by the oxidation of the 4-alkylanilines using 30% hydrogen peroxide (*31*). Recently, the synthesis of 4,4′-*n*-dialkyloxyazoxybenzenes by reductive coupling of 4-alkyloxynitrobenzene with metallic bismuth pellets in a stainless steel ball mill has been reported (*32*) but nitroarenes having alkoxy chain longer than eight carbons show unsatisfactory conversion.

The present method affords azoxy compounds as the major product by reduction of 4-alkyloxynitrobenzenes using a mixture of zinc dust and ammonium chloride as reducing agent in aqueous ethanol medium. This new synthetic method is economical, rapid and environment-friendly. However, this method is only useful for symmetrical azoxybenzenes and is not suitable for unsymmetrical systems. The detailed synthetic route is depicted in Scheme 1. The yields for the different members (n=1–14) of the series are given in Table 1.

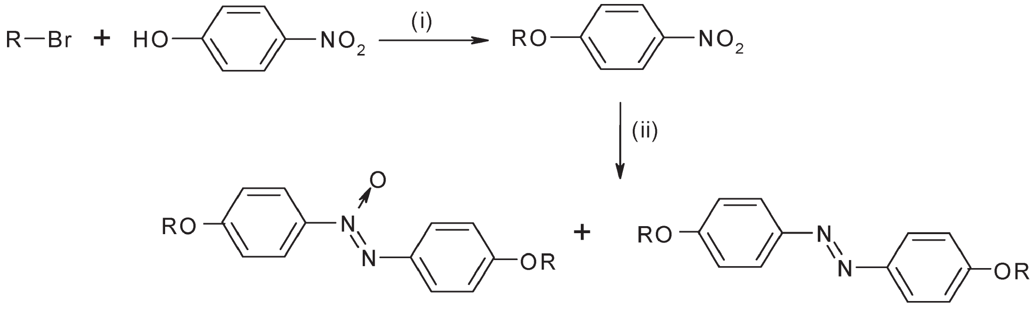
Mesogenic behaviour

The liquid crystalline behaviour of both new compounds (**1-13** and **1-14**) was studied using polarising optical microscopy and DSC. The observed transition temperatures and enthalpies are given in Table 2. As an example, the DSC thermogram of compound **1-13** is shown in Figure 1. Compound **1-13** exhibits solid-to-solid phase transitions, but no such transition is observed in **1-14**. The presence of two or more crystalline modifications is not uncommon among mesogens (*34*). Both the compounds exhibit a SmC phase with considerable supercooling. The thermal range of the SmC phase in both the compounds is quite large, i.e. 44.8 and 46.2°C, respectively. A schlieren texture during heating and a focal conic texture during cooling are observed in both compounds (*35*). The results of small-angle X-ray diffraction studies confirm the presence of the SmC phase, as was observed in other members of homologous series (*11, 19–21*).

Small-angle X-ray diffraction

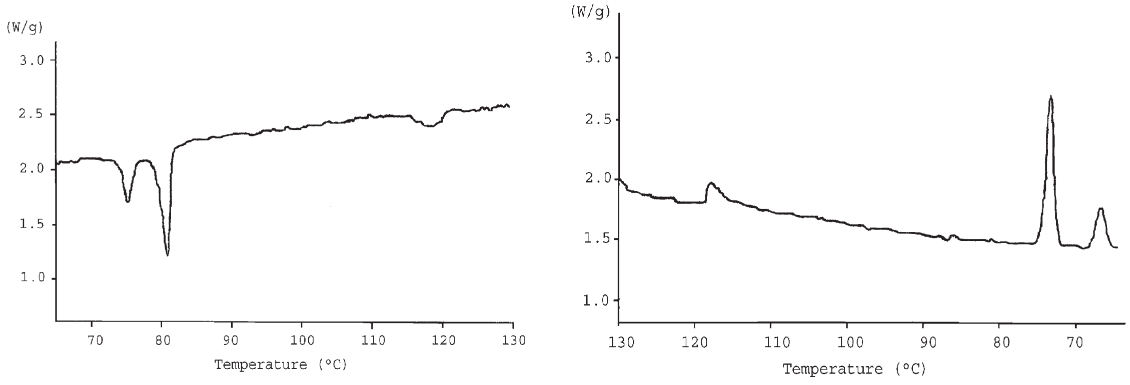
Small-angle X-ray diffraction studies were performed for **1-13** and **1-14** at room temperature and also at different temperatures within the mesogenic range. The desired temperature within the mesogenic range was attained by very slow and controlled cooling of the sample from the isotropic phase in the presence of a magnetic field of 3 kG. X-ray diffraction photographs at room temperature are displayed in Figure 2.

The existence of another solid phase in **1-13** was also revealed by X-ray studies. The *d*-spacings



1 **2**

Scheme 1. Synthesis of 4,4′-bis(*n*-alkoxy)azoxybenzenes: (i) anhydrous potassium carbonate, ethyl methyl ketone, reflux, 48 h; (ii) zinc powder (3 eq.), ammonium chloride (2 eq.), aqueous ethanol, 333 K, 1 h.



(*a*) (*b*)

Figure 1. DSC traces for compound **1-13** during (a) heating (b) cooling.

Table 2. Transition temperatures (°C) and transition enthalpies (Δ*H*, kJ mol^{-1}) for **1-13** and **1-14**.

Comp.	Cr_1	Heating (Δ*H*) Cooling (Δ*H*)	Cr_2	Heating (Δ*H*) Cooling (Δ*H*)	SmC	Heating (Δ*H*) Cooling (Δ*H*)	I
1-13	•	74.9 (10.34)	•	80.7 (25.01)	•	117.9 (7.54)	•
	•	66.5 (7.90)	•	72.9 (26.91)	•	117.7 (6.95)	•
1-14	•	84.6 (56.56)	–		•	117.6 (1.28)	•
	•	68.7 (53.10)	–		•	114.9 (3.87)	•

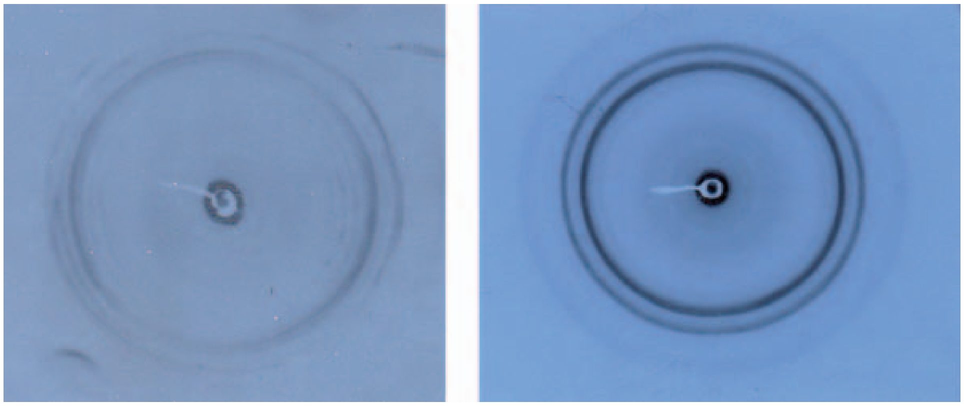
corresponding to diffraction rings observed in the Cr_2 phase (Figure 3) are different from those in the Cr_1 phase (Figure 2a).

The X-ray diffraction photographs of magnetically aligned samples are shown in Figures 4 and 5.

Diffractograms of both samples show small-angle sharp peaks associated with the smectic layer spacing and diffuse wide-angle peaks related to the degree of disorder within the smectic layers, showing liquid-like in-plane order. Non-orthogonal angles between the maxima of the two diffraction features are characteristic of a SmC phase.

The average intermolecular distance (*D*) at different temperatures was calculated from the peak positions of the outer equatorial arc in the diffraction pattern, using the modified Bragg formula $D=1.117\lambda/2\sin\theta$ derived on the basis of cylindrical symmetry (*36*). The *D* values for both compounds increase slightly with temperature (Figure 6, Table 3), indicating a decrease in the density of molecular packing.

The smectic layer spacing (*d*), determined from the meridional diffraction peaks using the Bragg relation, is found to be shorter than the calculated



(a) (b)

Figure 2. X-ray diffraction photograph of (a) **1-13** and (b) **1-14** at room temperature in the solid state.

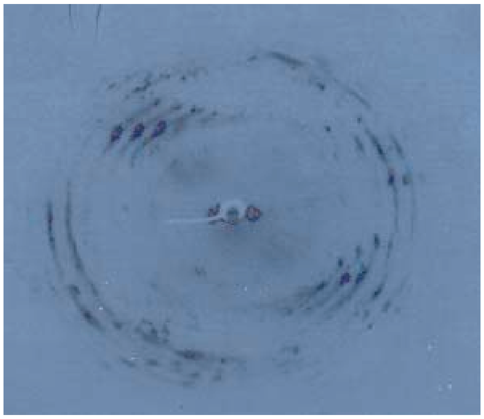


Figure 3. X-ray diffraction photograph of **1-13** at 65°C in a different solid state.

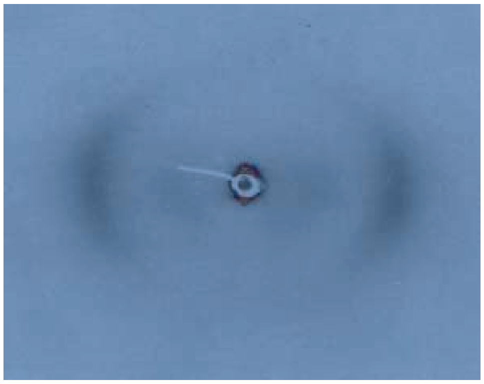


Figure 4. X-ray diffraction photograph of **1-13** at 80°C in the smectic phase during cooling.

molecular length (L) in the all-trans configuration for both the compounds. The d values are also found to decrease with temperature (Figure 7, Table 3). The observed d/L ratios for both compounds at all temperatures are considerably less than unity, similar to other members of this family (3), indicating that the molecules are tilted within smectic layers.

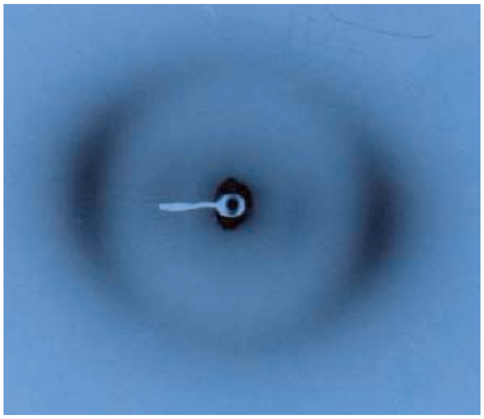


Figure 5. X-ray diffraction photograph of **1-14** at 105°C in the smectic phase during cooling.

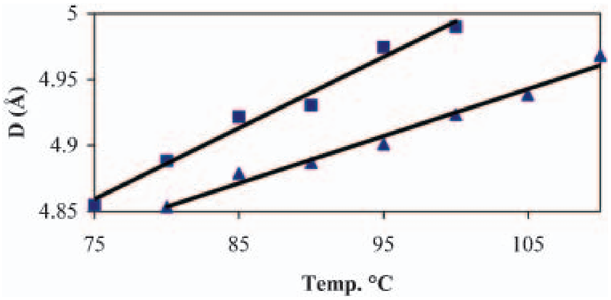


Figure 6. Variation of average intermolecular distance D with temperature for **1-13** (■) and for **1-14** (▲).

Table 3. Calculated molecular lengths, L, average intermolecular distances in the layers, D, smectic layer spacings, d, and calculated ratios, d/L.

Comp.	L /Å	D /Å	d /Å	d/L	Temp. /°C
1-13	45.39	4.85	30.6	0.675	75.0
		4.89	30.5	0.673	80.0
		4.92	30.3	0.668	85.0
		4.93	30.1	0.663	90.0
		4.97	29.9	0.658	95.0
		4.99	29.8	0.656	100.0
1-14	47.92	4.85	31.8	0.663	80.0
		4.88	31.6	0.660	85.0
		4.89	31.5	0.657	90.0
		4.90	31.2	0.651	95.0
		4.92	31.0	0.647	100.0
		4.94	30.7	0.641	105.0
		4.97	30.3	0.632	110.0

X-ray crystal structure

A full knowledge of the crystal and molecular structure of a liquid crystal-forming compound is important for a proper understanding of the structure and properties of the mesophases. The crystal structures of 4,4′-bis(n-alkoxy)azoxybenzenes have already been studied for other members (n=1, 2, 3, 5, 7 and 12) of the series (*15, 18, 37–40*). Recently, the crystal structure of 4,4′-bis(n-octyloxy)azoxybenzenes and its molecular aggregation have been reported (*33*).

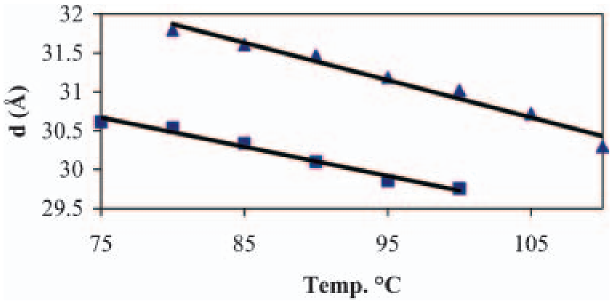


Figure 7. Variation of smectic layer spacing d with temperature for **1-13** (■) and for **1-14** (▲).

Table 4. Crystal and structure refinement data for compound **1-14**.

Empirical formula	$C_{40}H_{66}N_2O_3$
Formula weight	622.95
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a=7.4691(6) Å α=84.9030(10)°
	b=8.8665(7) Å β=89.6830(10)°
	c=27.834(2) Å γ=86.3250(10)°
Volume	1832.2(2) $Å^3$
Z, Calculated density	2, 1.129 mg m^{-3}
Absorption coefficient	0.070 mm^{-1}
F(000)	688
Crystal size	0.43 × 0.32 × 0.17 mm
Theta range for data collection	0.73 to 25.50°
Limiting indices	$-9 \le h \le 9$, $-10 \le k \le 10$, $-33 \le l \le 33$
Reflections collected/unique	13 903/6752 [R(int)=0.0543]
Completeness to theta=25.50	99.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6752/0/408
Goodness-of-fit on F^2	0.994
Final R indices [$I > 2\sigma(I)$]	R_1=0.0456, wR_2=0.1188
R indices (all data)	R_1=0.0589, wR_2=0.1300
Largest diff. peak and hole	0.280 and −0.350 e $Å^{-3}$

Attempts were made to grow single crystals of **1-13** and **1-14** by slow diffusion of ethanol into dichloromethane solutions of the compounds, but only crystals of **1-14** were found suitable for single-crystal X-ray diffraction study. The crystal and structure refinement data for compound **1-14** is summarised in Table 4.

The asymmetric unit of 4,4′-bis(*n*-tetradecyloxy) azoxybenzene is shown in Figure 8. Each paraffin chain has an all-trans conformation, which results in an almost planar zigzag chain. The unit cell packing diagram of compound **1-14** (Figure 9) shows that it has a tilted layer structure.

The N=N [1.274(2) Å] and N–O [1.279(2) Å] bond lengths of **1-14** are typical of trans aromatic azoxy compounds (*33, 41*). Three planar fragments in the molecular structure of **1-14** may be identified: the benzene ring (C1→C6) connected to N1(O2) (**A**), the azoxy group (**B**) and the other benzene ring (C21→C26) connected to N2 (**C**). The dihedral angles between different planes comprising **A/B, A/C** and **B/C** can be represented by the torsion angles N2−N1−C3−C2=5.90(16)°, C3−N1−N2−C23=−179.65(9)° and N1−N21−C23−C22=8.24(18)°, respectively. So the overall molecule is not planar. The benzene ring (**B**) connected with N2 is more twisted with respect to the azoxy group.

Two characteristic features of trans aromatic azoxy compounds appear in the geometry of the C23−N2−N1(O2)−C3 fragment. The C3−N1(O2) bond is longer than C23−N2 bond by about 0.052 Å. The bond angles within the C23−N2−N1(O2)−C3 fragment are expected to be close to 120° for trigonal sp^2 hybridisation, but the angles for N2−N1−O2 and N2−C23−C22 exceed this value by 7.8(1) and 8.61(10)°, respectively. This deformation is believed to originate from the steric interaction between atom O2 and the H atoms in the ortho positions (*42*).

The molecules are arranged parallel to each other and form a layer-like assembly where C–H···π interactions exist in between the centroids of the benzene C1–C6 (*Cg*1) and C21–C26 (*Cg*2) rings and the alkyl H atoms (Figure 10). The tilted layer formation (Figure 9) of the molecules in the solid state is believed to be the precursor of the SmC phase. There are no aromatic $\pi-\pi$ stacking interactions in **1-14**.

4. Conclusion

A simple method for the synthesis of 4,4′-bis(*n*-alkoxy)azoxybenzenes (*n*=1–14) by reduction of nitroarenes with benign and inexpensive zinc dust in a water–ethanol mixture has been developed. Two hitherto unknown members (*n*=13, 14) of the azoxy series have been characterised by polarising optical microscopy, DSC and small-angle X-ray diffraction techniques. Both new compounds exhibit a SmC phase and their mesomorphic range is quite large. Compound **1-13** shows two crystalline modifications. Small-angle X-ray diffraction studies show that the smectic layer spacing decreases with temperature, indicating an increase in molecular tilt. The intermolecular distance slightly increases with

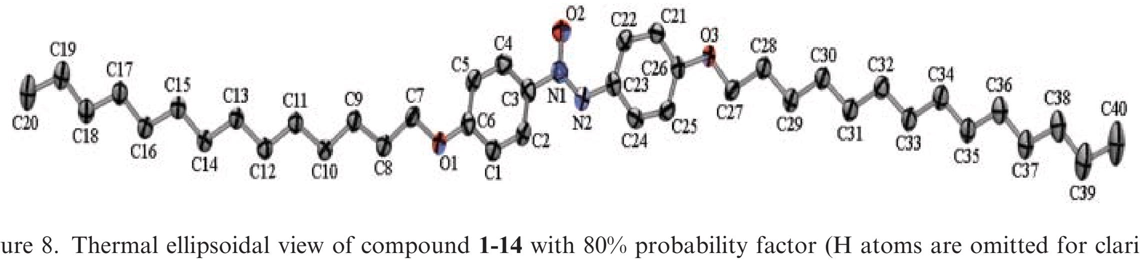


Figure 8. Thermal ellipsoidal view of compound **1-14** with 80% probability factor (H atoms are omitted for clarity).

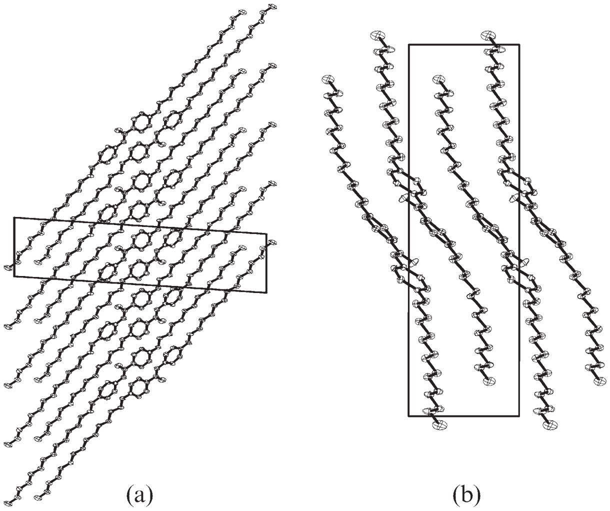


Figure 9. Unit cell packing diagram of compound **1-14** along (a) [100] and (b) [010].

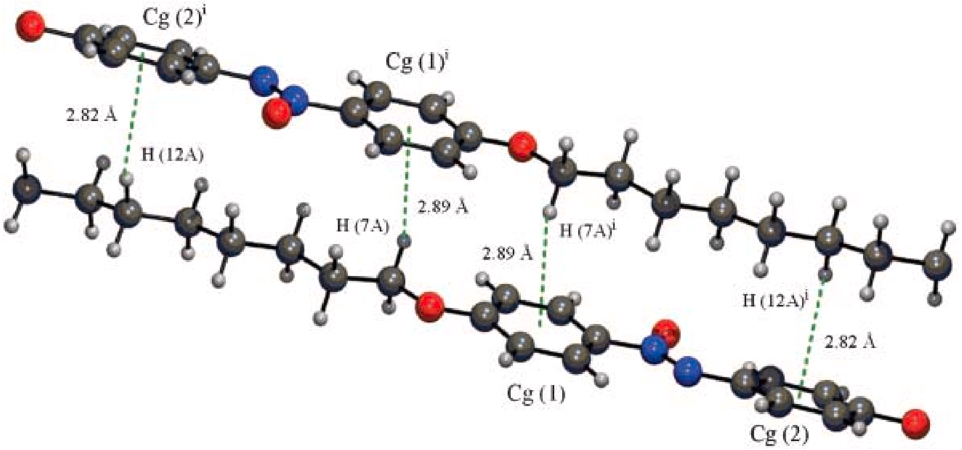


Figure 10. A representation of C–H···π interactions of **1-14** indicated by dashed lines (symmetry code: (i) $1-x,-y,1-z$; *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C21–C26 rings, respectively). Part of the alkyloxy chain is omitted for clarity.

temperature, suggesting a decrease in packing density. A single-crystal X-ray diffraction study of 4,4′-bis(*n*-tetradecyloxy)azoxybenzene reveals that C–H···π interactions are present in the molecular assembly. Tilted layer formation in the solid state is considered as the precursor of the SmC phase shown by the compound on melting.

Supplementary materials

Crystallographic data for structural analysis of **1-14** has been deposited at the Cambridge Crystallographic Data Centre, CCDC, No. 668705. 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).

Acknowledgements

Financial support (SR/S1/IC-08/2007) from DST, Government of India, is gratefully acknowledged. We thank CSIR (India) for the award of a fellowship (PD) and UGC (New Delhi) for Special Assistance Programme to our Department. We also thank Professor A. Ramanan, IIT Delhi, for X-ray data collection.

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