organic papers

Bis[4-(n-octyloxy)phenyl]diazene oxide

Purak Das,ᵃ Debatra Narayan Neogi,ᵃ Shailesh Upreti,ᵇ Pradip Kumar Mandalᶜ and Pinaki Bandyopadhyayᵃ*

ᵃDepartment of Chemistry, University of North Bengal, Siliguri 734 430, India, ᵇDepartment of Chemistry, Indian Institute of Technology, Delhi, New Delhi 110 016, India, and ᶜDepartment of Physics, University of North Bengal, Siliguri 734 430, India

Correspondence e-mail:
pbchem@rediffmail.com

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.071
wR factor = 0.200
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Zinc-ammonium chloride reduction of 4-(n-octyloxy)nitro-benzene in an aqueous ethanol has yielded the title compound, $C_{28}H_{42}N_2O_3$. There are two independent molecules in the asymmetric unit; one is in a disordered state, with two components in unequal proportions (60:40).

Comment

The title compound, (I), belongs to the 4,4′-di-n-alkoxy-azoxybenzene series which is well known for mesogenic behavior (Das *et al.*, 1999). Compound (I) exhibits a smectic C phase followed by a nematic phase on melting (Chistyakov & Chaikowsky, 1969). For a proper understanding of the structure and bonding of the mesophases, a full knowledge of the crystal and molecular structure of the liquid-crystal-forming compound is very useful. The crystal structures of 4,4′-di-n-alkoxyazoxybenzenes with alkyl chains C_nH_{2n+1} (n = 1–3, 5, 7 and 12) have been reported (Kubo *et al.*, 2005; Chebli & Brisse, 1995; Sciau *et al.*, 1988; Romain *et al.*, 1986; Shivaprakash *et al.*, 1985; Cotrait *et al.*, 1979). Although preliminary structural information on the nematic phase of (I) at 383 K has appeared in the literature (Chistyakov & Chaikovskii, 1973), the single-crystal X-ray analysis of (I) has not been reported so far. Against this background, we report here the crystal structure of (I).

(I)
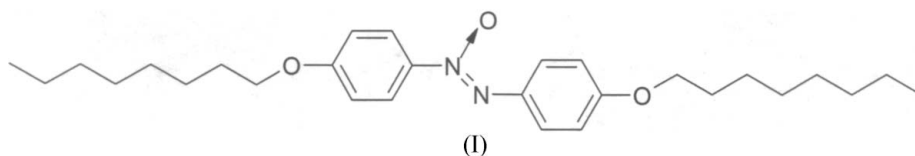
The asymmetric unit of (I) is shown in Fig. 1. There are two independent molecules, one of them having disorder in the azoxy group. They are related through a pseudo-twofold axis, which passes nearly through the azoxy group and is in the molecular plane. A very similar disorder has been observed in 4,4′-azoxydianisole (Chebli & Brisse, 1995). The disorder in the azoxy group in (I) can be explained by assuming that approximately 60% of the molecules in an $\alpha\beta$ orientation are superimposed on 40% of the molecules in a $\beta\alpha$ orientation (consider atom C29 as the α end and C56 as the β end). The N=N and N—O bond lengths (Table 1) of (I), derived from the non-disordered molecule, are typical of *trans* aromatic azoxy compounds (Ejsmont *et al.*, 2000). Two characteristic features of *trans* aromatic azoxy compounds appear in the geometry of the C12—N1—N2(O1)—C15 fragment. The C15—N2(O1) bond is longer than C12—N1 bond by *ca*
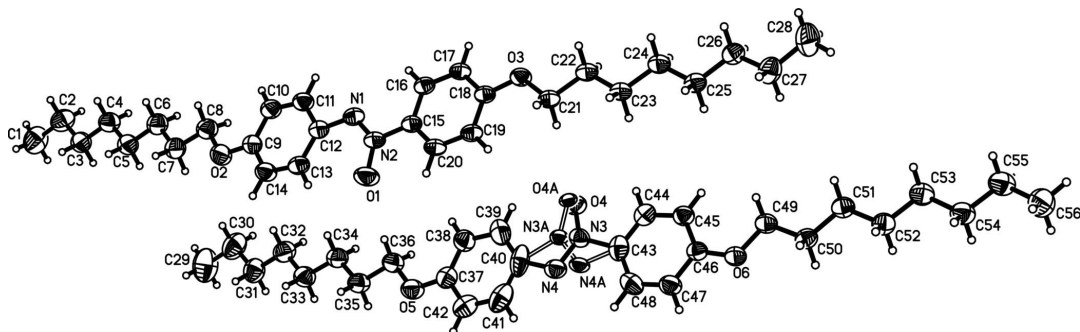
Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level. Both disorder components are shown.
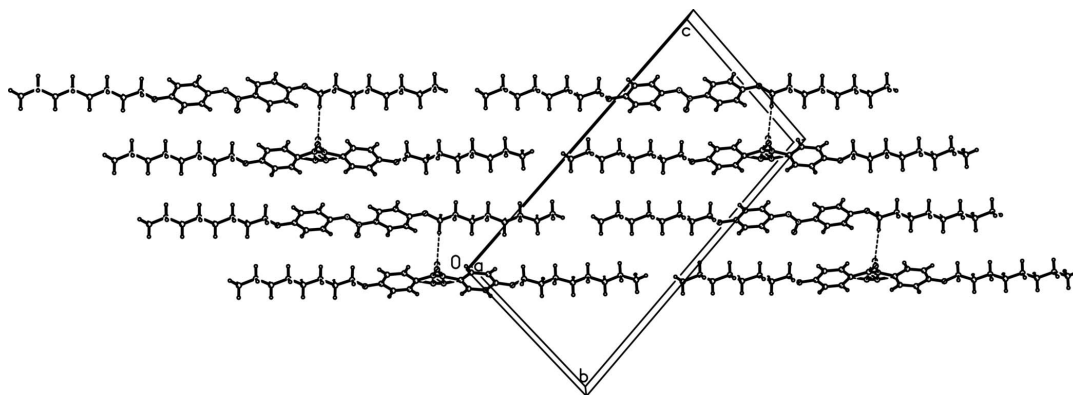

Figure 2
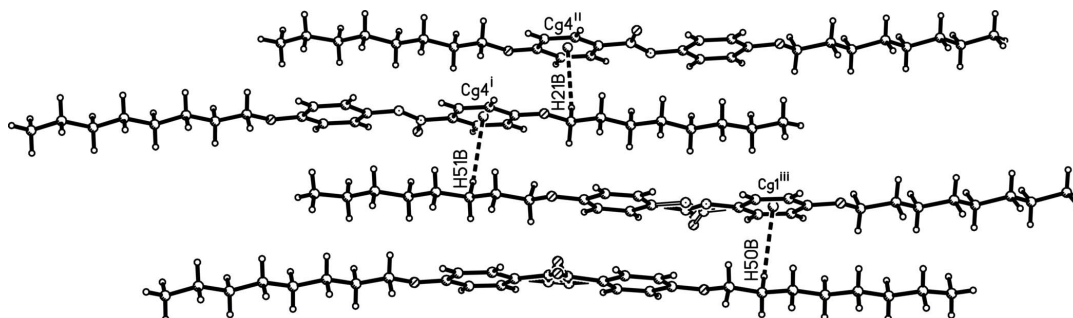The molecular arrangement of (I) in the *bc* plane. Dashed lines indicate C—H···O interactions.

Figure 3
A representation of the C—H···π interactions of (I), indicated by dashed lines. [Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) 1 − *x*, 1 − *y*, −*z*; (iii) 1 − *x*, −*y*, −*z*.]

0.036 Å. The bond angles within the C12—N1—N2(O1)—C15 fragment are expected to be close to 120° for trigonal sp^2 hybridization, but the angles for N1—N2—O1 and C13—C12—N1 exceed this value by 6.5 (2) and 9.5 (2)°, respectively (Table 1). This deformation is believed to originate from the steric interaction between atom O1 and the H atoms in the *ortho* positions (Ejsmont *et al.*, 2002).

The supramolecular aggregation of the molecules is ensured by weak C—H···O and C—H···π interactions (Table 2). In the *bc* plane, the molecules are arranged parallel to each other and form a layer-like assembly in which a weak C—H···O (C21—H21*A*···O4*A*) bond links the ordered and the disordered molecules, forming a pair (Fig. 2). Such a layer-like assembly is stacked one over the other along the *a* axis, held together by C—H···O (C45—H45···O4[i]) (see Table 2 for

symmetry code), as well as C—H···π interactions (Fig. 3). In the C—H···π interactions, the centroids of the benzene C15–C20 (*Cg*4) and C37–C42 (*Cg*1) rings are involved with the alkyl H atoms (Table 2). There are no aromatic π–π stacking interactions in (I).

Experimental

Although a number of synthetic routes towards arylazoxy compounds have been reported in the literature, we have developed the following procedure, which is particularly convenient for 4,4′-bis(*n*-alkoxy)azoxybenzene. To a solution of 4-(*n*-octyloxy)nitrobenzene (2.51 g, 10 mmol) in a mixture (100 ml) of ethanol and water (9:1 *v/v*), warmed to 333 K, ammonium chloride (1.07 g, 20 mmol) was added.

Further heating was stopped and zinc powder (1.96 g, 30 mmol) was added to the reaction mixture very slowly over 10 min with stirring. The reaction mixture was stirred for a further hour. The resulting reaction mixture was diluted with an equal volume of cold water and then filtered. The yellow residue mixed with zinc oxide was extracted with dichloromethane. Evaporation of the solvent afforded a yellow solid. The mixture was chromatographed on a silica-gel column. The first band containing 4,4′-bis(n-alkoxy)azobenzene was eluted with a mixture of benzene and petroleum ether (1:4 v/v; yield 0.096 g, 4.4%). The following band containing compound (I) was eluted with a mixture of benzene and petroleum ether (2:3 v/v). Complete evaporation of the volatiles under reduced pressure gave (I) as a pale-yellow solid (yield: 1.249 g, 55%). Suitable crystals of (I) were obtained by slow diffusion of a dichloromethane solution into aqueous ethanol.

Crystal data

$C_{28}H_{42}N_2O_3$	$Z = 4$
$M_r = 454.64$	$D_x = 1.113$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.9763$ (14) Å	Cell parameters from 4767
$b = 13.666$ (3) Å	reflections
$c = 26.241$ (5) Å	$\theta = 2.3–23.8°$
$\alpha = 93.706$ (3)°	$\mu = 0.07$ mm^{-1}
$\beta = 98.370$ (3)°	$T = 293$ (2) K
$\gamma = 105.294$ (3)°	Plate, pale yellow
$V = 2713.7$ (9) Å^3	$0.42 \times 0.18 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	9516 independent reflections
	6035 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 25.0°$
	$h = -9 \rightarrow 8$
$T_{min} = 0.970$, $T_{max} = 0.995$	$k = -16 \rightarrow 16$
19801 measured reflections	$l = -31 \rightarrow 31$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.071$	$+ 0.2585P]$
$wR(F^2) = 0.200$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
9516 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
607 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C12—N1	1.406 (3)	N2—O1	1.272 (2)
N1—N2	1.269 (2)	N2—C15	1.442 (3)
C13—C12—N1	129.5 (2)	N1—N2—O1	126.5 (2)
C13—C12—N1—N2	7.6 (4)	N1—N2—C15—C16	−5.7 (3)
C12—N1—N2—C15	176.99 (17)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C21—H21A$\cdots$O4A	0.97	2.58	3.535 (3)	167
C45—H45A$\cdots$O4^{i}	0.93	2.58	3.449 (3)	157
C21—H21B$\cdots$Cg4^{ii}	0.97	2.86	3.747 (3)	152
C50—H50B$\cdots$Cg1^{iii}	0.97	2.92	3.750 (3)	144
C51—H51B$\cdots$Cg4^{i}	0.97	2.89	3.757 (3)	149

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y, -z$.
Note: Cg1 and Cg4 are the centroids of the C37–C42 and C15–C20 rings, respectively.

Refinement of the site-occupancy factors for the disordered atoms N3, N4 and O4 gave the values 0.59 (2), 0.57 (3) and 0.55 (5), respectively; these factors were thereafter fixed at 0.60. The occupancy factors of the other possible set of positions (N3A/N4A/N4A) are 0.40. H atoms were treated as riding atoms, with C—H distances of 0.93 (aromatic) and 0.97 Å (aliphatic), and with U_{iso}(H) = $1.2U_{eq}$(C) (1.5U_{eq} for methyl groups).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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