Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Bis(4-dodecyloxyphenyl)diazene oxide

Kanji Kubo,[a]* Taisuke Matsumoto,[b] Akira Mori,[b] Hajime Takahashi[c] and Haruko Takechi[c]

[a]School of Dentistry, Health Sciences University of Hokkaido, 1757 Kanazawa, Ishikari-Tobetsu, Hokkaido 061-0293, Japan, [b]Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, and [c]Faculty of Pharmaceutical Sciences, Health Sciences University of Hokkaido, 1757 Kanazawa, Ishikari-Tobetsu, Hokkaido 061-0293, Japan

Correspondence e-mail:
kubo-k@hoku-iryo-u.ac.jp

Received 11 August 2005
Accepted 18 August 2005
Online 27 August 2005

Key indicators

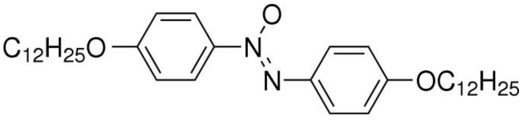
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.117
wR factor = 0.226
Data-to-parameter ratio = 20.1

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

The title compound, $C_{36}H_{58}N_2O_3$, also known as a liquid crystalline material, has a phase sequence of crystal–smectic C–isotropic liquid. The two benzene rings are nearly coplanar with the central NNO group, and each paraffin chain has an all-*trans* conformation. The molecules form a tilted layer structure *via* intermolecular π–π, C—H$\cdots$O and C—H$\cdots\pi$ interactions.

Comment

The synthesis, elucidation of crystal structures and investigation of physical properties of new liquid crystals are important for studying the relationship between molecular structures and mesophases (Kubo, 2004). Numerous studies have been dedicated to the structural investigation and the determination of the molecular aggregation mechanisms. X-ray crystallographic analysis plays an important role in obtaining information about intermolecular interactions controlling mesophases. We have also reported the crystal structures of some liquid crystals, such as 4-cyanophenyl 4-*n*-alkoxybenzoate (Kubo & Mori, 2001), *N*,*N*′-bis(5-alkoxytropon-2-yl)-piperazine (Yamamoto *et al.*, 2001), 2,2′-dialkoxy-5,5′-bitropone (Kubo, Sutoh *et al.*, 2002; Kubo *et al.*, 2004), 5-nitro-2-(4-alkoxybenzoylamino)tropone (Kubo, Tsuruta *et al.*, 2002) and bis(tropon-2-yl)-4,4′-azobisbenzoate (Kubo, Mori *et al.*, 2005). Series of azoxybenzene derivatives have been widely studied as useful mesogens with simple molecular structure. Mesomorphic sequences of dialkyloxyazoxybenzene (DnAB) are dependent on the length of the alkoxy chains OC_nH_{2n+1}, *viz.* crystal–nematic–isotropic for n = 1–5, crystal–smectic C–nematic–isotropic for n = 6–10, and crystal–smectic C–isotropic for n = 12 (Vill, 2004). The crystal structures of DnAB with shorter alkyl chains (n = 1–3, 5 and 7) have been reported (Chebli & Brisse, 1995; Sciau *et al.*, 1988; Romain *et al.*, 1986; Shivaprakash *et al.*, 1985; Cotrait *et al.*, 1979). We now report the structure of 4,4′-didodecyloxyazoxybenzene (D12AB), (I), which has an enantiotropic smectic C phase, with the aim of contributing to a deeper understanding of the relationships between mesomorphic properties and molecular packing in the crystal structure.



(I)

Each paraffin chain has an all-*trans* conformation (Fig. 1), thus forming an almost planar zigzag chain; the deviations of atoms from the least-squares planes defined by atoms C7–C18

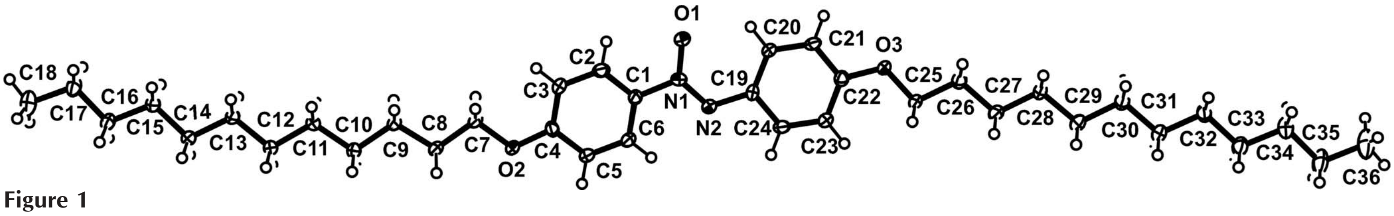


Figure 1
Molecular structure of (I), showing 50% probability displacement ellipsoids.

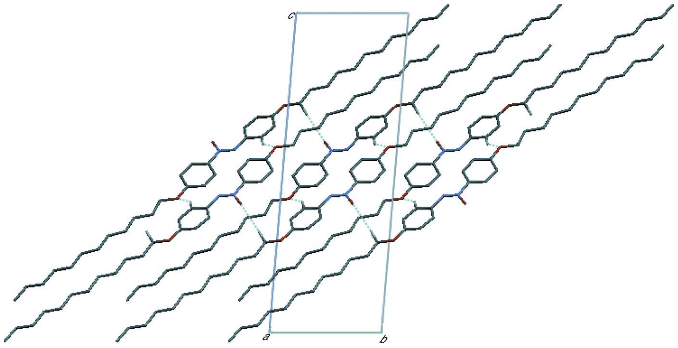


Figure 2
Packing diagram of (I) viewed down the *a* axis. The broken lines indicate C—H···O interactions. H atoms have been omitted unless these are involved in the weak hydrogen bonding.

and C25–C36 are all within 0.120 (5) and 0.057 (5) Å, respectively. The molecular length of the compound is 41.595 (6) Å for the C18···C36 distance. The two benzene rings are nearly coplanar with the central NNO group. The dihedral angles between the least-squares planes *A* (defined by C1–C6) and *B* (defined by C19–C24), and between the least-squares planes *A* and *C* (defined by N1, N2 and O1) are 13.5 (1) and 6.2 (2)°, respectively, resembling those (13.1 and 4.0°) of D7AB (Cotrait *et al.*, 1979) and distinct from those (2.3 and 4.0°) in D3AB (Romain *et al.*, 1986).

Compound (I) has a tilted layer structure (Fig. 2). The crystal structure is consistent with the packing model in the smectic C phase. Intermolecular π–π interactions between the azoxybenzene dimer planes is observed (Fig. 3). The distance between intermolecular azoxybenzene planes is 3.286 (3) Å for C5···C20^{i} [symmetry code: (i) $1 - x, 1 - y, 1 - z$], which is within the range associated with π–π interactions (3.3–3.8 Å; Prout *et al.*, 1973; Kubo *et al.*, 2001; Kubo, Matsumoto & Mori, 2005). The value is shorter than that [3.386 (3) Å] of the intermolecular contact in 7-diethylamino-3-dimethylamino-coumarin (Takahashi *et al.*, 2005).

There are intermolecular C—H···O and C—H···π interactions (Table 2 and Fig. 2). The H33···O2^{ii} [symmetry code: (ii) $2 - x, 1 - y, 1 - z$] and H34···O1^{iii} distances [symmetry code: (iii) $x, 1 + y, z$] are close to the typical C—H···O distance (2.5–2.7 Å; Kubo *et al.*, 1997; Meadows *et al.*, 2000; Kubo, Matsumoto & Mori, 2005). For the C—H···π interaction, the H7···C2^{iv} [symmetry code: (iv) $2 - x, -y, 1 - z$] distance is 2.873 Å, which agrees with typical C—H···π distances (2.8–3.1 Å; Saragai *et al.*, 2001; Matsumoto *et al.*, 2002).

Experimental

Compound (I) was commercially available (Tokyo Kasei Kogyo Co. Ltd, Japan), and was purified by repeated recrystallization from hexane and ethyl acetate solution (1:1 *v*/*v*). Crystals of (I) were grown from a chloroform solution by slow evaporation.

Crystal data

$C_{36}H_{58}N_2O_3$
$M_r = 566.84$
Triclinic, $P\bar{1}$
$a = 7.514$ (7) Å
$b = 8.853$ (8) Å
$c = 25.21$ (2) Å
$\alpha = 85.15$ (2)°
$\beta = 89.36$ (2)°
$\gamma = 86.19$ (2)°
$V = 1667$ (3) Å^3
$Z = 2$
$D_x = 1.129$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2246 reflections
$\theta = 3.2$–27.5°
$\mu = 0.07$ mm^{-1}
$T = 123.1$ K
Platelet, yellow
0.15 × 0.10 × 0.04 mm

Data collection

Rigaku Saturn diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.778$, $T_{\max} = 0.997$
21767 measured reflections
7497 independent reflections
4191 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.077$
$\theta_{\max} = 27.6°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.117$
$wR(F^2) = 0.226$
$S = 1.21$
7466 reflections
371 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 2.294P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

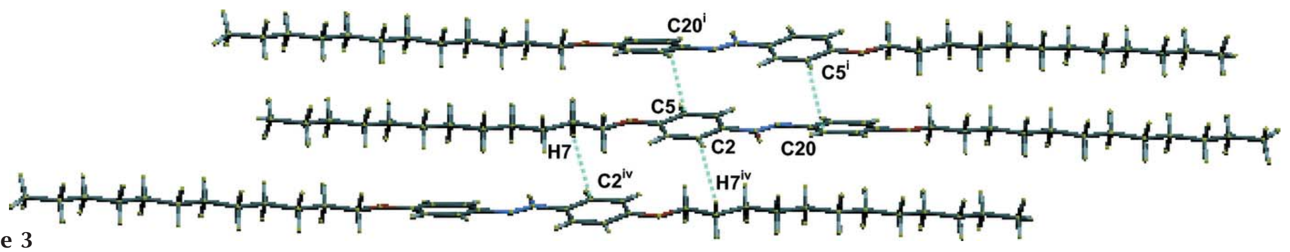


Figure 3
The π–π and C—H···π interactions for (I), indicated by dotted lines. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, -y, 1 - z$.]

Acta Cryst. (2005). E**61**, o3056–o3058 Kubo *et al.* • $C_{36}H_{58}N_2O_3$ **o3057**

Table 1
Selected geometric parameters (Å, °).

O1—N1	1.270 (3)	C3—C4	1.392 (4)
O2—C4	1.364 (3)	C4—C3	1.392 (4)
O3—C22	1.370 (4)	C4—C5	1.395 (4)
N1—N2	1.280 (4)	C5—C6	1.379 (4)
N1—C1	1.464 (4)	C19—C20	1.405 (4)
N2—C19	1.417 (4)	C19—C24	1.403 (4)
C1—C2	1.384 (4)	C20—C21	1.375 (4)
C1—C6	1.390 (4)	C21—C22	1.396 (4)
C2—C3	1.387 (4)	C22—C23	1.386 (4)
C3—C2	1.387 (4)	C23—C24	1.386 (4)
C5···C20^{i}	3.286 (4)		
O1—N1—N2	127.6 (3)	C1—N1—N2	115.4 (2)
O1—N1—C1	117.0 (2)	N1—N2—C19	119.9 (2)
C7—O2—C4—C3	4.6 (4)	C12—C13—C14—C15	−179.9 (2)
C7—O2—C4—C5	−175.5 (2)	C13—C14—C15—C16	179.1 (2)
C4—O2—C7—C8	178.1 (2)	C14—C15—C16—C17	179.2 (2)
C25—O3—C22—C21	179.3 (2)	C15—C16—C17—C18	−179.5 (3)
C25—O3—C22—C23	−1.9 (4)	O3—C25—C26—C27	−179.6 (2)
C22—O3—C25—C26	−177.0 (2)	C25—C26—C27—C28	−178.7 (2)
O1—N1—N2—C19	−2.0 (4)	C26—C27—C28—C29	−179.6 (2)
C1—N1—N2—C19	179.8 (2)	C27—C28—C29—C30	−178.6 (2)
O2—C7—C8—C9	179.6 (2)	C28—C29—C30—C31	−179.9 (2)
C7—C8—C9—C10	−176.9 (2)	C29—C30—C31—C32	179.7 (2)
C8—C9—C10—C11	−172.1 (2)	C30—C31—C32—C33	179.0 (3)
C9—C10—C11—C12	179.8 (2)	C31—C32—C33—C34	178.4 (3)
C10—C11—C12—C13	−176.5 (2)	C32—C33—C34—C35	−179.5 (3)
C11—C12—C13—C14	179.0 (2)	C33—C34—C35—C36	177.8 (3)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C24—H33···O2^{ii}	0.93	2.71	3.532 (4)	148 (1)
C25—H34···O1^{iii}	0.97	2.68	3.648 (4)	173 (1)
C8—H7···C2^{iv}	0.97	2.87	3.646 (4)	137 (1)

Symmetry codes: (ii) $-x+2, -y+1, -z+1$; (iii) $+x, +y+1, +z$; (iv) $-x+2, -y, -z+1$.

H atoms were included in the refinement at calculated positions as riding atoms, with C—H set to 0.93 Å for aromatic, 0.96 Å for CH_3 and 0.97 Å for CH_2 H atoms, and with $U_{iso}(H) = 1.2U_{eq}(C)$. Some low-angle reflections were excluded from the refinement, as they were probably obscured by the beam stop.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *CrystalStructure*.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I ., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Chebli, C. & Brisse, F. (1995). *Acta Cryst.* C**51**, 1164–1167.

Cotrait, M., Marsau, P. & Pesquer, M. (1979). *Acta Cryst.* B**35**, 1102–1107.

Jacobson, R. (1998). Private communication to the Rigaku Corporation.

Kubo, K. (2004). *Kagaku*, **59**, 56–57.

Kubo, K., Kato, N. & Sakurai, T. (1997). *Acta Cryst.* C**53**, 132–134.

Kubo, K., Matsumoto, T. & Mori, A. (2005). *Acta Cryst.* E**61**, o2542–o2544.

Kubo, K. & Mori, A. (2001). *Acta Cryst.* E**57**, o113–o115.

Kubo, K., Mori, A., Ujiie, S. & Tschierske, C. (2004). *J. Oleo Sci.* **53**, 575–579.

Kubo, K., Mori, A., Ujiie, S. & Tschierske, C. (2005). *J. Oleo Sci.* **54**, 179–183.

Kubo, K., Sutoh, T., Mori, A. & Ujiie, S. (2002). *Bull. Chem. Soc. Jpn*, **75**, 1353–1358.

Kubo, K., Tsuruta, T., Hashimoto, M., Mori, A. & Ujiie, S. (2002). *ITE Lett. Batteries New Tech. Med.* **3**, 475–478.

Kubo, K., Yamamoto, E. & Mori, A. (2001). *Acta Cryst.* C**57**, 611–613.

Matsumoto, A., Tanaka, T., Tsubouchi, T., Tashiro, K., Saragai, S. & Nakamoto, S. (2002). *J. Am. Chem. Soc.* **124**, 8891–8902.

Meadows, E. S., De Wall, S. L., Barbour, L. J., Fronczek, F. R., Kim, M.-S. & Gokel, G. W. (2000). *J. Am. Chem. Soc.* **122**, 3325–3335.

Prout, C. K., Orley, T. M., Tickle, I. J. & Wright, J. D. (1973). *J. Chem. Soc. Perkin Trans. 2*, pp. 523–527.

Rigaku (1999). *CrystalClear*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Rigaku/MSC & Rigaku (2004). *CrystalStructure*. Version 3.7.0. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Romain, F., Gruger, A. & Guilhem, J. (1986). *Mol. Cryst. Liq. Cryst.* **135**, 111–128.

Saragai, S., Tashiro, K., Nakamoto, S., Matsumoto, A. & Tsubouchi, T. (2001). *J. Phys. Chem. B*, **105**, 4155–4165.

Sciau, P., Lapasset, J. & Moret, J. (1988). *Acta Cryst.* C**44**, 1089–1092.

Shivaprakash, N. C., Abdoh, M. M. M. & Prasad, J. S. (1985). *Z. Kristallogr.* **172**, 79–87.

Takahashi, H., Takechi, H., Kubo, K. & Matsumoto, T. (2005). *Acta Cryst.* E**61**, o3061–o3063.

Vill, V. (2004). *LiqCryst 4.5.* Fujitsu Kyushu System Engineering, Fukuoka, Japan.

Yamamoto, E., Kubo, K., Mori, A. & Ujiie, S. (2001). *Chem. Lett.* pp. 100–101.

o3058 Kubo *et al.* • $C_{36}H_{58}N_2O_3$ *Acta Cryst.* (2005). E**61**, o3056–o3058