Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

1,14-Dibromotetradecane

Kenjiro Uno* and Naotake Nakamura

Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan

Correspondence e-mail:
rc002961@se.ritsumei.ac.jp

Received 11 April 2003
Accepted 22 April 2003
Online 30 April 2003

Key indicators

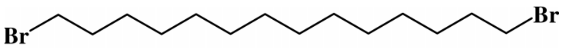
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
R factor = 0.043
wR factor = 0.099
Data-to-parameter ratio = 21.1

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

In the title compound, $C_{14}H_{28}Br_2$, the molecule is centrosymmetric and the molecular skeleton, including both terminal Br atoms, has an all-*trans* conformation. In the crystal structure, the molecules form layers in which the long axes of the molecules are inclined with respect to the layers. The molecules are arranged in a zigzag manner in the neighboring layers, making a herring-bone motif just as in the tilt–smectic C phase of liquid crystals.

Comment

Normal long-chain aliphatic compounds such as *n*-alkanes, α-monosubstituted *n*-alkanes, and α,ω-disubstituted *n*-alkanes, have been investigated in order to disclose some principles of organic chemical crystallography and basic polymer science, because the molecular skeleton consists of a simple, all-*trans*, zigzag extended hydrocarbon chain. The molecular shape of these compounds can be regarded as rod-like, which is one of the typical features of molecules in liquid crystals; the molecules in the crystalline state form a layered structure similar to those of the smectic liquid crystalline phase. Moreover, some of them exhibit a high-temperature rotator phase just below their melting points, in which molecules have orientational freedom in some degree as well as that in liquid crystals. Therefore, normal long-chain aliphatic compounds have also been investigated as models for smectic liquid crystals.



(I)

Previously, many researchers have studied the crystal structures of many different kinds of normal long-chain aliphatic compounds, for example, *n*-alkanes (*e.g.* Nyburg & Gerson, 1992), *n*-primary alcohols (*e.g.* Michaud *et al.*, 2000), and α,ω-disubstituted *n*-alkanes such as 1,12-dibromododecane (Kulpe *et al.*, 1981) and 11-bromoundecan-1-ol (Rosen & Hybl, 1972). Recently, we have systematically analysed the crystal structures of alkane-α,ω-diols containing 10–19 and 21–23 C atoms (Nakamura *et al.*, 2001; Uno *et al.*, 2002), and we have studied the phase-transition phenomena of the series of alkane-α,ω-diols containing 13–24 C atoms (Ogawa & Nakamura, 1999). In addition, we have also analyzed the crystal structures of 1,16-dibromohexadecane (Kobayashi *et al.*, 1995) and 1,18-dibromooctadecane (Nakamura *et al.*, 1993) in order to elucidate the effect of the terminal groups in normal, long-chain aliphatic compounds. Against this background, we have carried out the crystal structure analysis of 1,14-dibromo-

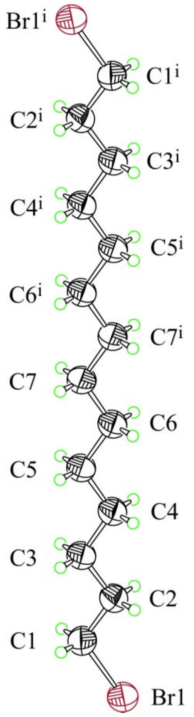


Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme [symmetry code: (i) $2 - x, -y, -z$]. Displacement ellipsoids are drawn at the 50% probability level.

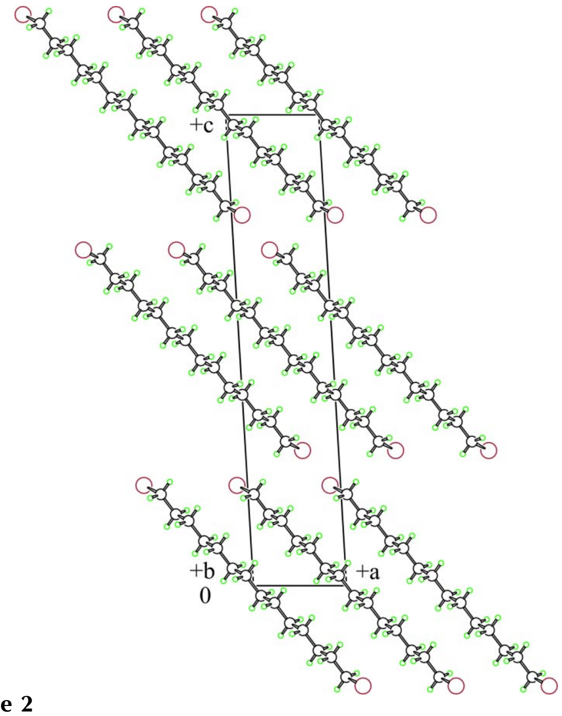


Figure 2
The projection of the crystal structure of (I) along the *b* axis.

tetradecane, (I). In this paper, the crystal structure of (I) is described and compared with those of the homologous series and analogous compounds.

The molecular structure of (I) is shown in Fig. 1. The molecule is centrosymmetric and all torsion angles are close to ±180°, that is, the molecular skeleton, including both terminal Br atoms, has an all-*trans* conformation. Fig. 2 shows the projection of the crystal structure of (I) along the *b* axis. The molecules form layers with a thickness of *c*/2. In the layer, the long axes of the molecules are inclined at 37.9 (1)° with respect to the line normal to the basal plane of Br atoms, the *ab* plane. This layer structure is similar to those of the triclinic structures of the even-numbered *n*-alkanes containing 6–24 C atoms, but the inclination angle of (I) is larger than those of the even-numbered *n*-alkanes [*e.g.* *n*-icosane: 18.5 (1)°; Nyburg & Gerson, 1992]. We believe that the arrangement in the layer is influenced by the steric and electrostatic repulsion of the Br atoms at both ends. As a result, the molecular position in the layer is shifted along the direction of the long axis of the neighboring molecule.

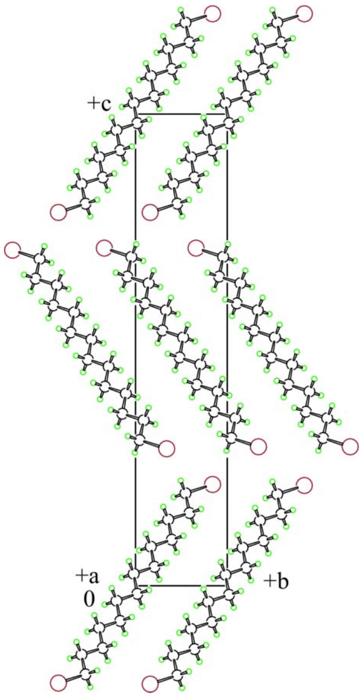


Figure 3
The projection of the crystal structure of (I) along the *a* axis.

The repulsion also influences the interlayer arrangement, so that the molecules between the molecules in neighboring layers swivel on their long axis, with a dihedral angle of the *trans* zigzag planes of 30.1 (2)°. Moreover, the molecules are arranged in a zigzag manner between adjacent layers, making a herringbone motif, just as in the tilt–smectic C phase of liquid crystals, as shown in Fig. 3. The layers are stacked closely in such a way that the α-CH$_2$ groups are allowed to fit into the grooves formed by Br atoms, with shortest contacts of 3.758 (3) Å, agreeing closely with the van der Waals contact of 3.75 Å (Rowland & Taylor, 1996). Such a close packing is also observed in the even-numbered alkane-α,ω-diols containing 4–18 and 22 C atoms (*e.g.* Thalladi *et al.*, 2000).

The features in the molecular and crystal structure of (I) are similar to those of the homologous series with an even number of C atoms, *viz*. 1,12-dibromododecane (Kulpe *et al.*, 1981), 1,16-dibromohexadecane (Kobayashi *et al.*, 1995), and 1,18-dibromooctadecane (Nakamura *et al.*, 1993).

Experimental

The title compound, (I), was synthesized from commercially available 1,14-tetradecanedioic acid (Tokyo Kasei Kogyo Co. Ltd) by esterification, reduction, and bromination. The pure compound was obtained through fractional distillation and recrystallization. The single crystal of (I) used for the X-ray analysis was grown by slow evaporation of a solution in a mixture of *n*-heptane and 2-propanol (1:3).

Crystal data

$C_{14}H_{28}Br_2$
$M_r = 356.16$
Monoclinic, $P2_1/n$
$a = 5.486$ (6) Å
$b = 5.389$ (7) Å
$c = 27.827$ (4) Å
$\beta = 93.38$ (4)°
$V = 821.2$ (14) Å^3
$Z = 2$
$D_x = 1.440$ Mg m^{-3}
Cu Kα radiation
Cell parameters from 22 reflections
$\theta = 9.6$–19.9°
$\mu = 6.06$ mm^{-1}
$T = 296$ (1) K
Plate, colorless
0.43 × 0.43 × 0.08 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{\min} = 0.208$, $T_{\max} = 0.782$
2304 measured reflections
1563 independent reflections
1305 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 70.1°$
$h = -6 \rightarrow 1$
$k = 0 \rightarrow 6$
$l = -33 \rightarrow 33$
1 standard reflection every 150 reflections
intensity decay: 2.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.099$
$S = 1.00$
1563 reflections
74 parameters
H-atom parameters constrained
$w = 1/[0.0002F_o^2 + 8.4\sigma^2(F_o) + 0.21]/(4F_o^2)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 24.8 (2)

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.947 (5)	C4—C5	1.507 (6)
C1—C2	1.490 (5)	C5—C6	1.520 (5)
C2—C3	1.509 (6)	C6—C7	1.510 (6)
C3—C4	1.523 (5)	C7—C7$^{\rm i}$	1.508 (7)
Br1—C1—C2—C3	−179.3 (3)	C4—C5—C6—C7	179.4 (4)
C1—C2—C3—C4	−180.0 (4)	C5—C6—C7—C7$^{\rm i}$	179.8 (5)
C2—C3—C4—C5	179.6 (4)	C6—C7—C7$^{\rm i}$—C6$^{\rm i}$	180.0
C3—C4—C5—C6	179.8 (4)		

Symmetry code: (i) $2 - x, -y, -z$.

Table 2
Contact distances (Å).

Br1···Br1$^{\rm i}$	3.758 (3)	Br1···Br1$^{\rm ii}$	3.758 (3)

Symmetry codes: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

All H atoms were located at idealized positions (C—H = 0.95 Å) and made to ride on their parent C atoms. The H-atom isotropic displacement parameters were set to be 1.2 $U_{\rm eq}$ of the parent C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2001); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.

Kobayashi, H., Yamamoto, T. & Nakamura, N. (1995). *Cryst. Res. Technol.* **30**, 275–280.

Kulpe, S., Seidel, I., Szulzewsky, K., Steger, U. & Steger, E. (1981). *Cryst. Res. Technol.* **16**, 349–356.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall and C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Michaud, F., Ventolà, L., Calvet, M. T., Cuevas-Diarte, M. A., Solans, X. & Font-Bardía, M. (2000). *Acta Cryst.* C**56**, 219–221.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation & Rigaku (2001). *CrystalStructure*. Version 3.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Nakamura, N., Uno, K. & Ogawa, Y. (2001). *Acta Cryst.* E**57**, o1091–o1093, and references therein.

Nakamura, N., Yamamoto, T., Kobayashi, H. & Yoshimura, Y. (1993). *Cryst. Res. Technol.* **28**, 953–957.

Nyburg, S. C. & Gerson, A. R. (1992). *Acta Cryst.* B**48**, 103–106.

Ogawa, Y. & Nakamura, N. (1999). *Bull. Chem. Soc. Jpn*, **72**, 943–946.

Rosen, L. S. & Hybl, A. (1972). *Acta Cryst.* B**28**, 610–617.

Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.

Thalladi, V. R., Boese, R. & Weiss, H. C. (2000). *Angew. Chem. Int. Ed.* **39**, 918–922.

Uno, K., Nakamura, N. & Ogawa, Y. (2002). *Acta Cryst.* A**58**, C-338.

Watkin, D. J., Prout, C. K., Carruthers, R. J. & Betteridge, P. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.