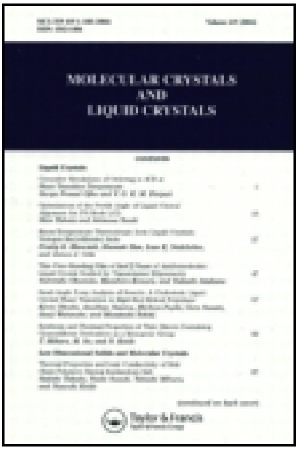
This article was downloaded by: [University of Haifa Library]
On: 16 August 2012, At: 08:46
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Hexyltrimethylammonium Bromide Inclusion Complex With Rac-1,1′-Bi-2-Naphthol

Emmanuel Marfo-owusu [a], Kenji Okuyama [a] & Keiichi Noguchi [a]

[a] Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184-8588, Japan

Version of record first published: 24 Sep 2006

To cite this article: Emmanuel Marfo-owusu, Kenji Okuyama & Keiichi Noguchi (2000): Hexyltrimethylammonium Bromide Inclusion Complex With Rac-1,1′-Bi-2-Naphthol, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 339:1, 73-82

To link to this article: http://dx.doi.org/10.1080/10587250008031033

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

Mol. Cryst. Liq. Cryst., Vol. 339, pp. 73-82
Reprints available directly from the publisher
Photocopying permitted by license only

© 2000 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

Hexyltrimethylammonium Bromide Inclusion Complex With Rac-1,1′-Bi-2-Naphthol

EMMANUEL MARFO-OWUSU, KENJI OKUYAMA* and
KEIICHI NOGUCHI

Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184–8588, Japan

(Received May 07, 1999; In final form June 27, 1999)

The crystal structure of 1:1 inclusion complex of hexyltrimethylammonium bromide (6TAB) and rac-1, 1′-bi-2-naphthol (BNP) was analysed by the X-ray diffraction method. It was shown that the bromide anion participates in a hydrogen bond with one of the OH groups of BNP (O1···Br, 3.22(1)Å). The bromide anion also plays a role as the hydrogen acceptor of the OH group of the water molecule (OW···Br, 3.21(3)Å). A strong hydrogen bond was found between the other OH group of BNP and oxygen of the water molecule (O2···OW, 2.63(3)Å). The short C-H···C distances between hydrogen atoms of the alkyl chain together with the methyl groups and carbon atoms of the aromatic rings suggested C-H···π interactions. The atomic distances shorter than the sum of the van der Waals radius (2.97Å) were C10···H6 2.85Å, C14···H9 2.83Å, and C16···H11 2.88Å. The X-ray powder diffraction studies on the complex suggested that the complex crystals can be obtained by crystallization from the solution and also by mixing powdered samples in a mortar.

Keywords: Hexyltrimethylammonium bromide; Inclusion complex; Racemic compound; Crystal structure; Non-planar aromatic; Molecular interactions

INTRODUCTION

Recently, it was reported that amphiphilic onium salts such as ammonium and phosphonium salts form inclusion complexes with alcohol and phenol derivatives via hydrogen bond formation between the counter anion of the host onium cation and the hydroxyl group of the guest alcohol or phenol [1]. In these complex formations, molecular recognition between the host and guest occured and

---

* Corresponding author. Tel. :-81–423–88–7028. Fax:-81–423–88–7209. e-mail: okuyamak@cc.tuat.ac.jp

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

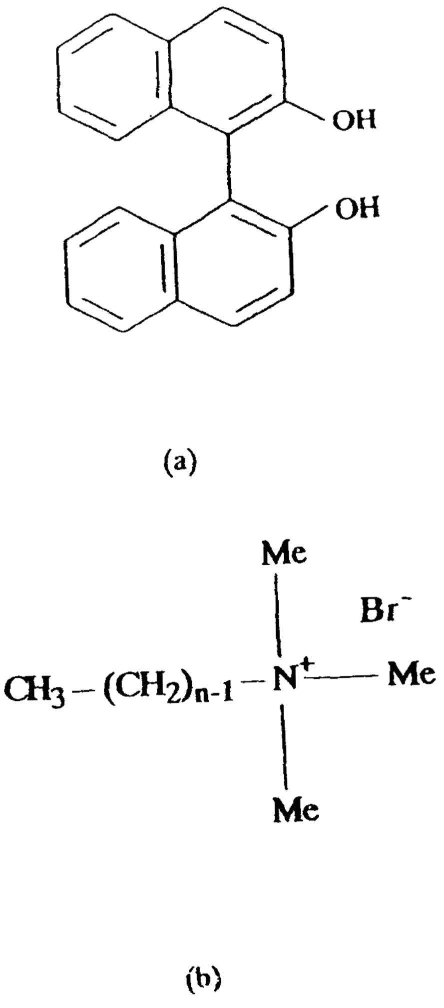


FIGURE 1 Chemical structures of host amphiphile and guest aromatic molecule. (a) Guest aromatic molecule: Rac-1,1′-Bi-2-naphthol (BNP) (b) Host amphiphiles: n = 6, Hexyltrimethylammonium Bromide (6TAB)

separation of isomers of the guest was accomplished [1]. Interestingly, the formation of the inclusion complexes can be achieved by crystallization from solution and also by mixing powdered samples in a mortar [2]. In these inclusion complexes it has been observed that most of the amphiphilic molecules take very similar two-dimensional smectic layers in the solid state. The smectic layers stack along the direction normal to the layer surface to make a three dimensional crystal structure. The molecular arrangement in the smectic layer depends on the chemical structure of an element amphiphile. A typical case is observed in dialkyldimethylammonium salts, in which amphiphiles form a bimolecular layer with some tilt to compensate for the difference of cross-sections between the hydrophilic head part and the hydrophobic tail part [3,4]. Meanwhile, in the cases of monoalkyltrimethylammonium salts [5], alkyl chains from both sides of the layer surfaces are usually packed together in an interdigitating manner and tilt against the layer surface to compensate for the large hydrophilic head part.

It has been found that, when a chiral onium salt interacts with a racemic compound a successful enantiomeric resolution is accomplished [6]. For example, rac.-1,1′ -bi-2-naphthol (hereafter, BNP) was easily resolved by complexation with N-benzylcinchonidinium chloride, because this chiral onium salt forms a 1:1 inclusion complex with (R)-(+)-1,1′-bi-2-naphthol (hereafter, RBNP) selectively [6]. So far, the inclusion ability of a monoalkyltrimethylammonium halide with chiral or racemic guest molecules has not been reported yet. We have been successful in obtaining 1:1 inclusion complexes of ammonium salts with short alkyl chains adducts with BNP and RBNP. The inclusion ability of hexyltrimethylammonium bromide (hereafter, 6TAB) with either BNP or RBNP attracts attention to investigate the host-guest molecular recognition in these complexes and investigate further the probable optical resolution of BNP using a monoalkytrimethylammonium halide. Achieving the selective recognition of (+) or (-)-BNP by an amphiphilic molecule constitutes an important difficult task which is very challenging to the supramolecular chemist. Due to the industrial and pharmaceutical needs of chiral compounds, exploitation of economically acceptable optical resolution methods is a subject of considerable recent development.

In our paper presented earlier on, we reported on the crystal structure of 6TAB with RBNP [8] but in this paper the crystal structure of the 6TAB inclusion complex with BNP will be discussed. The 6TAB and BNP molecules are termed as *host* and *guest* molecules respectively.

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

EXPERIMENTAL AND CRYSTAL STRUCTURE DETERMINATION

Preparation of Hexyltrimethylammonium Bromide Complex with rac-1, 1′-bi-2-naphthol

The 6TAB was purchased from Tokyo Chemical Industry Co.Ltd, whilst the BNP was purchased from Wako Chemical Industry Ltd, Tokyo, Japan.

The 6TAB complex with BNP (hereafter, 6TAB/BNP) was prepared by treating 6TAB with BNP in the molar ratio of 1:1 in an ethylacetate/acetone (2ml/8ml) solvent mixture. The mixture was simultaneously stirred and warmed at 30–40°C for 20 mins. This was then covered with perforated plastic thin wrap and kept in an incubator at 20°C for 4–6 days to obtain colourless needle-like single crystals. The crystals were removed from their viscous solutions and cleaned with diethylether and kept for X-ray diffraction studies.

X-ray Powder Diffraction

The X-ray diffraction of powdered samples of the host/guest mixture (6TAB/BNP) was measured by a Rigaku RAD-C diffractometer operated at 40kV and 30mA and with a scan speed of 10°/min. The X-ray powder diffraction patterns (Figure 2) for the powdered sample of the 6TAB complex was compared with simulated powder patterns based on atomic coordinates of the respective single crystals. The simulated powder pattern was performed by using the teXsan crystallographic software package of the Molecular Structure Corporation [9].

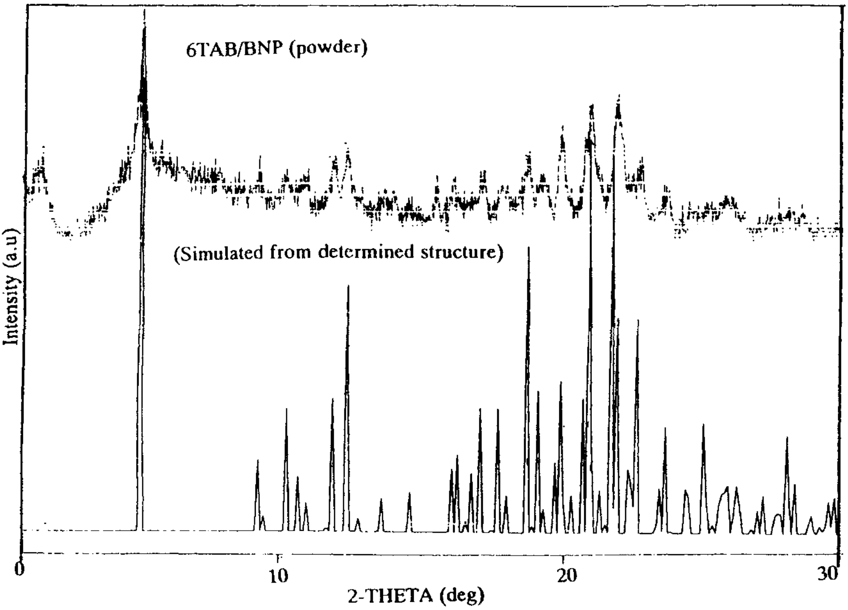


FIGURE 2 X-ray powder diffraction patterns of mixed powdered sample and simulated powder patterns of 6TAB/BNP

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

Intensity Data Collection

The determination of the unit cell dimensions and collection of the X-ray intensity data for the complex crystal were carried out using a four-circle diffractometer (Rigaku AFC5R) fitted with graphite monochromatized CuKα radiation ($\lambda = 1.5418Å$). The cell constants and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range of $78.98<2\theta<79.82°$. The intensity data was collected at 298K in the ω-2θ scan mode with a scanning speed of 8°/min and a scanning width of $\Delta\omega = (1.68 + 0.30 \tan\theta)°$. Three reference reflections were measured after every 100 reflections. No decay correction was applied to the intensity data. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data was corrected for Lorentz and polarization effects. The parameters for data collection and crystal data for the complex crystal are summarised in Table I.

TABLE I Crystal data and data collection details for the 6TAB/BNP complex

Molecular Formular	$C_9H_{22}N^+Br^-\cdot O\cdot C_{20}H_{12}O_2$
Formular Weight	524.50
Space group	$P\bar{1}$
a/Å	10.217(1)
b/Å	16.953(2)
c/Å	9.0924(9)
α/°	93.461(10)
β/°	111.126(8)
γ/°	105.806(10)
Volume/Å^3	1391.2(3)
Z	2
Dcalc /g cm^{-3}	1.25
F(000)	548
Crystal dimensions /mm	0.20 × 0.20 × 0.15
μ(CuKα)/cm^{-1}	22.3
Maximum 2θ/°	120
No. of Reflections Measured	Total: 4415 Unique: 4143
No. of Observed Reflections Used for Refinement	1805 ($I>2\sigma(I)$)
R-factor	0.085
Rw	0.386
Goodness-of-fit	1.97

Determination and Refinement of the Crystal Structure

The crystal structure was solved by direct method (SIR92) [10] and expanded using Fourier technique (DIRDIF94) [11]. The non-hydrogen atoms were refined anisotropically. Since the hydrogen atoms attached to O1, 02, and OW could not find their position in the difference Fourier map, they were not included in the calculation. All the other hydrogen atoms were introduced by geometrical calculations but not refined.

Bond lengths in the 6TAB molecule were restrained during refinement calculations. All C-C bonds were restrained to 1.520Å with weight 0.001, and the four N-C bonds to 1.490Å with weight 0.001. The atomic distances between C1···C2, C1···C3, C1···C4, C2···C3, C2···C4, C4···C6, C5···C7, C6···C8, and C7···C9 were restrained to 2.520Å with weight 0.001 to maintain appropriate values for bond angles in the host molecule. The crystal structure was refined by the full-matrix least-squares method (SHELXL-93) [12]. The R-value of 0.085 was obtained for 1805 observed reflections, 307 variable parameters and 19 geometrical restraints. The function minimised was $\Sigma w(F_o^2-F_c^2)^2$ where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$. and $a = 0.0973$, $b = 1.1944$, $P = (F_o^2 + 2F_c^2)/3$. The goodness of fit was 1.97. The maximum and minimum peaks on the final-difference Fourier map corresponded to 0.30 and $-0.29e^-/\text{Å}^3$, respectively. All the calculations performed during data processing, crystal structure analyses were done using teXsan software package for crystal structure analysis of the Molecular Structure Corporation [9]. The final fractional atomic coordinates, anisotropic thermal parameters, bond lengths and angles and tables of observed and calculated structure factors for the complex have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

RESULTS AND DISCUSSION

Powder Diffraction Pattern of 6TAB/BNP Complex

Most of the strong peaks in the powder diffraction patterns (Figure 2) correspond to the peaks in the simulated diffraction patterns, which suggest that the complex crystal can be obtained by crystallization from solution and also by mixing powdered samples in a mortar. The molecular structure and atomic numbering scheme for the complex is shown in Figure 3.

Crystal Structure of 6TAB/BNP Complex

The packing structure and crystal data of the complex are shown in Figure 4 and Table I respectively. The host/guest ratio of the complex is 1:1.

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

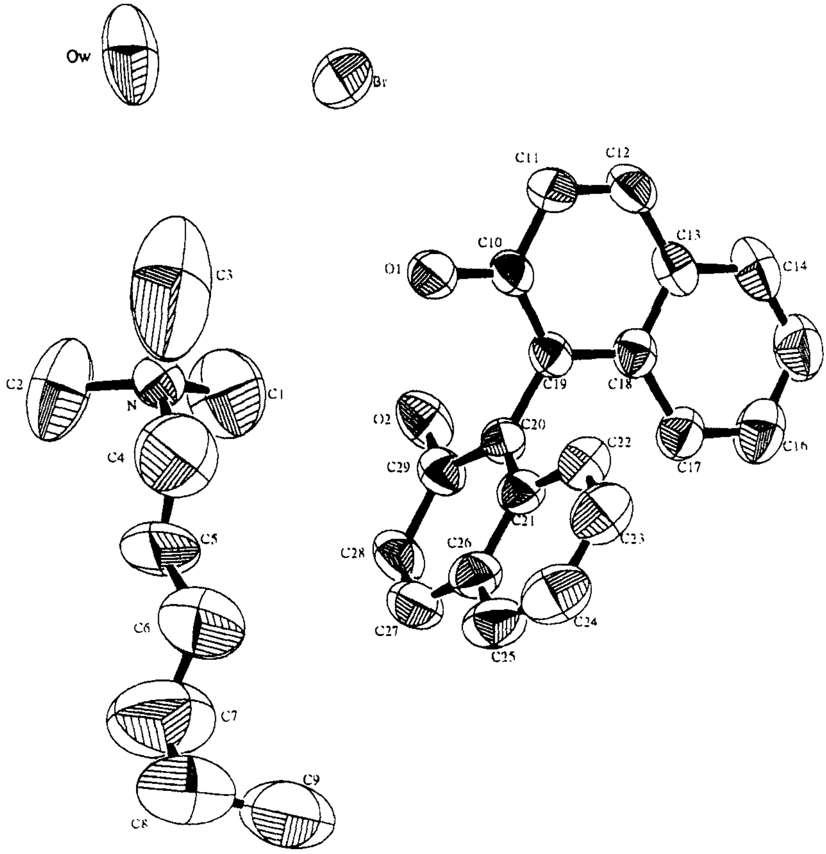


FIGURE 3 Molecular structure and atomic numbering of 6TAB/BNP. The 40% probability ellipsoids are shown. Hydrogen atoms are omitted for clarity of the structure

Molecular Conformation

The dihedral angles in the alkyl chain part are in the range of 180 ± 25° with the exception of C6-C7-C8-C9 [-64(8)°]. In Figure 3, it is observed that C3 has a larger temperature factor than other carbon atoms in the host and guest molecules. The observed temperature factor for the carbon atoms in 6TAB molecule indicate significant thermal motion of atoms in the 6TAB molecule. In the 6TAB molecule, the average bond lengths and angles are : 1.52(5)Å for the C-C bond, 112(3)° for the C-C-C angle, 1.53(3)Å for the N-C bond, and 109.2(2)° for C-N-C angle. In the naphthol moieties all the C-C, C-O bond lengths, C-C-C bond angles and C-C-C-C dihedral angles showed similar values found in (±)

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

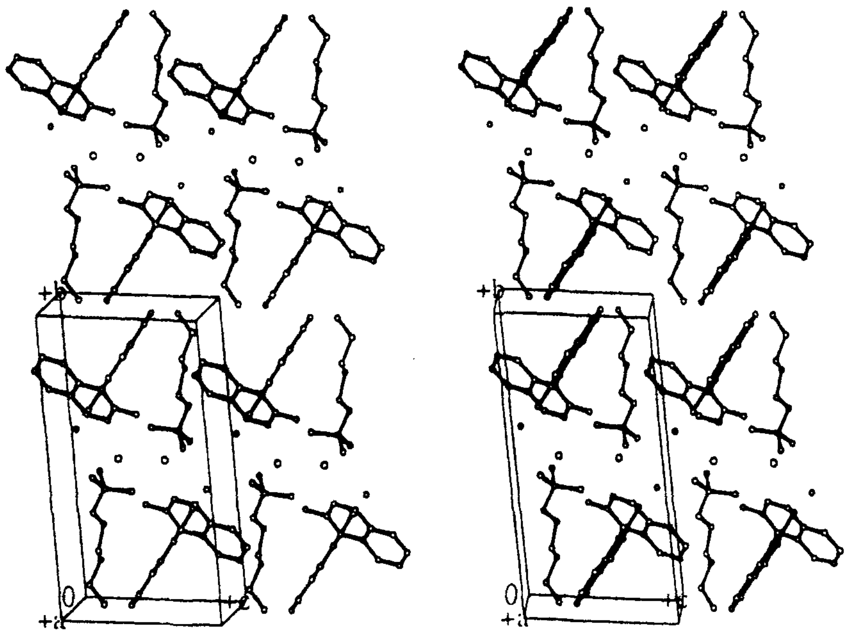


FIGURE 4 Stereo drawing of 6TAB/BNP viewed along the a-axis

–1,1′-bi-2-naphthol [13]. The dihedral angle between the two naphthol planes defined by O1,C10,...,C19 and O2,C29,...,C20 in BNP is 87.1(1)°. The mean deviations from the planarities of these naphthol moieties are 0.0111(1) and 0.0168(2)Å, respectively.

Crystal Packing and Host-Guest Interactions

The crystal packing arrangement of 6TAB/BNP viewed along the *a*-axis is illustrated in Figure 4. The bromide anion participates in a hydrogen bond (Figure 5) with one of the OH groups of BNP (O1···Br, 3.22(1)Å). The bromide anion also provides the hydrogen acceptor of the OH group of the water molecule (OW···Br, 3.21(3)Å). A strong hydrogen bond was found between the other OH group of BNP and oxygen of the water molecule (O2···OW, 2.63(3)Å. The short C-H···C distances between hydrogen atoms of the alkyl chain together with methyl groups and carbon atoms of the aromatic rings suggested an existence of C-H···π interactions (Figure 5). The atomic distances shorter than the sum of the van der Waals radius (2.97Å) are C10···H6 2.85Å, C14···H9 2.83Å, and C16···H11 2.88Å.

Downloaded by [University of Haifa Library] at 08:46 16 August 2012

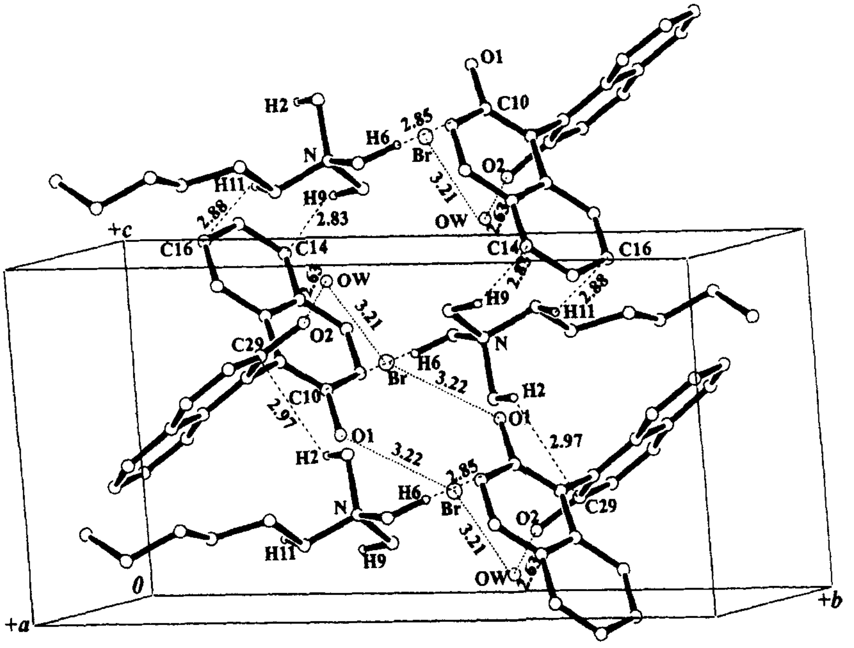


FIGURE 5 The C-H···π interactions, and hydrogen bonds observed in the 6TAB/BNP complex. The broken lines represent C-H···π interactions, whilst the dotted lines represent hydrogen bonds

Acknowledgements

The author E.Marfo-Owusu,wishes to express his gratitude to the Ministry of Culture, Science, Sports, and Education of Japan for awarding him the Monbusho Scholarship.

References

[1] F.Toda, K.Tanaka, T.Okada, S.A. Bourne, and L.R. Nassimbeni, Supramol.Chem., **3**, 291(1994).

[2] K. Okuyama,T. Ishii, K. Vongbupnimit and K. Noguchi, Mol.Cryst.Liq.Cryst., **312**,101–115 (1998).

[3] K. Okuyama, Y. Soboi, N.Iijima, K.Hirabayashi, T. Kunitake and T. Kajiyama, Bull.Chem.Soc.Jpn., **61**, 1485 (1988).

[4] K. Okuyama, N.Iijima, K.Hirabayashi, T.Kunitake and M. Kusunoki, Bull.Chem.Soc. Jpn., **61**, 2337 (1988).

[5] K.Noguchi, K.Okuyama, and K.Vongbupnimit, Mol.Cryst.Liq.Cryst., **276**, 185–191 (1996).

[6] K.Tanaka, T.Okada and F.Toda, Angew. Chem.Int.Ed.Engl., **32**, 1147(1994).

[7] F.Toda, K.Tanaka, Chem.Commun.,1087 (1997).

[8] E. Marfo-Owusu, K.Noguchi, and K. Okuyama, Mol.Cryst.Liq.Cryst., in press.

[9] TeXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

[10] SIR92: A. Altomore, A. Burla, M.C. Camalli, M. Cascarano, M. Giacovazzo, C. Guagliardi, G. Polidori. J.Appl.Cryst., **27**, 435 (1994).

[11] DIRDIF 94: P.T. Beurskens, G. Admiral, G. Beurskens, R. Israel, J.M.M. Smits (1994). The DIRDIF 94 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

[12] SHELXL-93: G.M. Sheldrick (1993). Program for the Refinement of Crystal Structures. University of Goettingen, Germany.

[13] K. Mori, Y. Masuda, S. Kashino.,Acta Crystallogr., **C49**, 1224 (1993).

Downloaded by [University of Haifa Library] at 08:46 16 August 2012