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

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Version of record first published: 24 Sep 2006

To cite this article: Emmanuel Marfo-owusu, Kenji Okuyama & Keiichi Noguchi (2000): The Hexadecyltrimethylammonium Chloride Inclusion Complex with Rac-1,1′-Bi-2-Naphthol, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 348:1, 227-237

To link to this article: http://dx.doi.org/10.1080/10587250008024808

Mol. Cryst. Liq. Cryst., Vol. 348, pp. 227-237
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The Hexadecyltrimethylammonium Chloride Inclusion Complex with Rac-1,1′-Bi-2-Naphthol

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(Received August 03, 1999; In final form October 12, 1999)

The crystal structure of 1:1 inclusion complex of hexadecyltrimethylammonium chloride (16TAC) with rac-1,1′-bi-2-naphthol (BNP) [a = 47.968(2), b = 8.757(2), c = 18.249(2)Å, β = 100.772(6)°, *C2/c*, R = 0.075 for 2578 observed reflections] was determined by the X-ray diffraction method. In the crystal structure there is a strong hydrogen bond between one of the OH groups of BNP and the oxygen of water molecule (O1···OW, 2.665(3)Å). The chloride anion acts as the hydrogen acceptor of the OH group of the water molecule (OW···Cl^-, 3.105(3)Å), and of the second OH group of BNP (O2···Cl^-, 3.108(2)Å). The short C-H···C distances between hydrogen atoms of the alkyl carbon atom together with one of the methyl groups, and carbon atoms in one of the naphthol rings indicated an existence of C-H···π interactions. The hydrophobic long alkyl chain of the 16TAC molecule contributes to the unique molecular packing arrangement observed in the 16TAC/BNP complex. The alkyl chain of the 16TAC molecule in this crystal is bent at C10 and does not exhibit the complete zig-zag planes as reported on the 16TAC crystal. The BNP molecules are completely trapped between the 16TAC molecules, and the interdigitated arrangement of the 16TAC molecules are clearly observed in the *ac*-plane. The X-ray powder diffraction studies on the mixed powdered samples of 16TAC and BNP suggested that the complex can be obtained by crystallization from the solution and also by mixing powdered samples in a mortar.

Keywords: Hexadecyltrimethylammonium chloride; Molecular complex; Crystal structure; Inclusion complex; Racemic compound

INTRODUCTION

Understanding of the molecular assembly provides an insight into molecular recognition studies. A crystal structure is built by a net of interactions among the

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molecules. Examples of important intermolecular interactions that are involved in the formation of a supramolecule are the hydrogen bonds, van der Waals interactions and metal-ligand coordination. It has been found that amphiphilic molecules such as monoalkyltrimethylammonium halide salts can be crystallized with various aromatic compounds to form crystalline inclusion complexes [1]. The formation of the complexes can also be prepared by mixing powdered samples of the amphiphilic compound and the aromatic compound in a mortar. In some of the amphiphilic-aromatic compound systems, the solution exhibits remarkable viscoelastic behaviour even in a very diluted state [2]. The solution of hexadecyltrimethylammonium bromide (hereafter, 16TAB) and salicyclic acid is one of the most typical systems [3]. In this system, the existence of elongated rod-like micelles which seem to cause the high viscoelasticity has been observed in electron micrographs [4,5]. The electron diffraction studies suggested the formation of a complex crystal between 16TAB and salicyclic acid [3]. In these inclusion complexes it has been observed that most of the amphiphilic molecules take a very similar two-dimensional layered structures in the solid state. The two-dimensional layered structures stack along the direction normal to the layer surface to make a three-dimensional crystal structure.

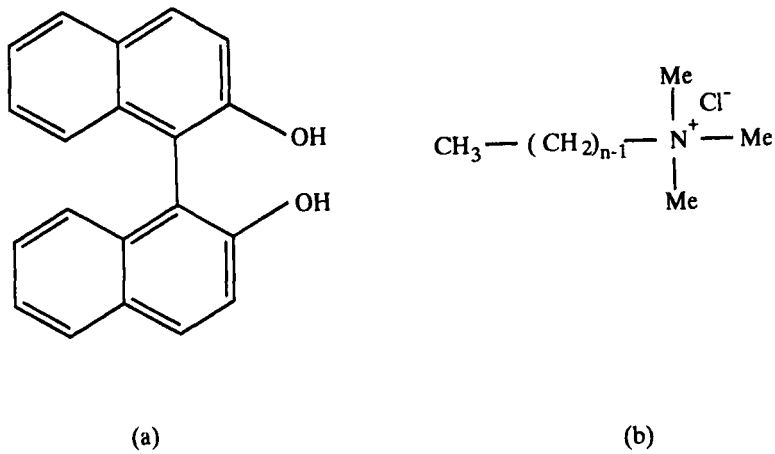

FIGURE 1 Chemical structures of host amphiphile and guest aromatic molecule. (a) Guest aromatic molecule: Rac-1,1′-Bi-2-naphthol (BNP) (b) Host amphiphile: n = 16, Hexadecyltrimethylammonium chloride (16TAC)

So far, until our recent reports [6,7], no work had ever been reported on the complex formation between monoalkyltrimethylammonium halide salts and chiral or racemic aromatic organic compounds. In these two papers, we reported on the molecular complexes of hexyltrimethylammonium bromide (6TAB) with

either (R)-(+)-1,1′ -bi-2-naphthol (hereafter, RBNP) or rac-1,1′-bi-2-naphthol (hereafter, BNP) and decyltrimethylammonium bromide (10TAB) with BNP [6,7]. In order to know whether the hydrophobic alkyl chain length is a factor for complex formation, and also contributes to changes in molecular packing and molecular interactions in complexes of these types, we are challenged to investigate the crystal complexes of both short and long hydrophobic alkyl chain amphiphilic compounds with chiral or racemic aromatic organic compounds for the purpose of understanding the molecular recognition phenomena in these inclusion complexes. Based on the success and understanding of our studies, we may further investigate the probable resolution of racemic compound using a non-chiral monoalkyltrimethylammonium halide salt. In this paper, we will discuss the crystal structure of inclusion complex of hexadecyltrimethylammonium chloride (hereafter, 16TAC) with BNP (hereafter, 16TAC/BNP). The 16TAC (long alkyl chain amphiphile) molecule is termed as the *host* molecule whilst the BNP molecule is termed as the *guest* molecule.

EXPERIMENTAL AND CRYSTAL STRUCTURE DETERMINATION

Preparation of the Hexadecyltrimethylammonium Chloride Complex with Rac-1,1′-Bi-2-naphthol

The 16TAC sample was purchased from Tokyo Chemical Industry Co.Ltd, whilst the rac-1,1′-bi-2-naphthol (BNP) was purchased from Wako Chemical Industry Ltd, Tokyo, Japan. The 16TAC complex with BNP (16TAC/BNP) was prepared by treating 16TAC with BNP in 8ml acetone solution. The mixture was simultaneously stirred and warmed at 30–40°C for 20mins in a glass bottle. The resulting warmed mixture was then covered with perforated plastic thin wrap and kept in an incubator at 20°C for 2 days to obtain colourless needle-like single crystals. The crystals obtained were removed from their viscous solutions and cleaned with diethylether and used for X-ray diffraction studies.

X-ray Powder Diffraction

The X-ray diffraction of a powdered sample of the host/guest complex was measured by a Rigaku RAD-C diffractometer operated at a 40kV and 30mA condition and with a scan speed of 10°/min. The X-ray powder diffraction pattern (Figure 2) for the powdered sample of the 16TAC/BNP complex was compared with the simulated powder pattern based on atomic coordinates of the structure analysed by this study. The simulated powder pattern was performed by using the teXsan crystallographic software package of the Molecular Structure Corporation [8].

X-ray Intensity Data Collection

The determination of the unit cell dimensions and collection of the X-ray intensity data of 16TAC/BNP was carried out using a four-circle diffractometer (Rigaku AFC5R) fitted with graphite monochromatized CuKα radiation ($\lambda = 1.5418$Å). The cell constants and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 23 carefully centered reflections in the range of $53.49<2\theta<77.93°$. The intensity data was collected at 298K in the ω-2θ scan mode with a scanning speed of 8°/min and scanning width of $\Delta w = (1.57 + 0.30 \tan\theta)°$. Three reference reflections were measured after every 100 reflections. Since a significant intensity decrease (1.81%) was observed, decay correction was applied to the intensity data. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were also corrected for Lorentz and polarization effects. The parameters for data collection and crystal data are summarized in Table I.

TABLE I Crystal data and data collection details for the 16TAC/BNP complex

Molecular Formular	$C_{39}H_{58}O_3N^+Cl^-$
Formular Weight	624.35
Space group	*C2/c*
a/Å	47.968(2)
b/Å	8.757(2)
c/Å	18.249(2)
α/°	90
β/°	100.772(6)
γ/°	90
Volume /Å^3	7530(1)
Z	8
Dcalc /g cm^{-3}	1.10
F(000)	2720
Crystal dimensions /mm	0.20 × 0.20 × 0.20
μ(CuKα) /cm^{-1}	11.55
Maximum 2θ /°	130.2
No. of Unique Reflections Measured	6898
No. of Observed Reflections Used for Refinement	2578 (I>2.5σ(I))
R-factor	0.075
Rw	0.066
Goodness-of-fit	1.84

Determination and Refinement of the Crystal Structure

The crystal structure of 16TAC/BNP complex adduct was solved by direct methods (SIR92) [9] and expanded using Fourier techniques (DIRDIF94) [10]. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to O(1), O(2) and OW were obtained from the difference Fourier map and refined isotropically. All the other hydrogen atoms were introduced by geometrical calculations and they were not refined.

Bond lengths in the 16TAC molecule were restrained during refinement calculations. All C-C bonds were restrained to 1.520Å with weight 0.001. The atomic distances between C4···C6, C6···C8, C8···C10, C10···C12 and C12···C14, C14···C16, C16···C18, and C17···C19 were restrained to 2.520Å with weight 0.001 to maintain appropriate values for bond angles in the host molecule. The final cycles of full-matrix least-squares refinement of 16TAC/BNP were based on 2578 observed reflections, 413 variable parameters and 23 geometrical restraints. The function minimized was $\Sigma\, w(|F_o|-|F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The final R-values were R = 0.075 and Rw = 0.066 respectively. The goodness of fit was 1.84. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.15 and $-0.15 e^-/Å^3$ respectively. All the calculations were performed during data processing and crystal structure analysis was done using the teXsan software package for crystal structure analysis of the Molecular Structure Corporation [8]. Neutral atomic scattering factors were taken from Cromer and Waber [11].

RESULTS AND DISCUSSION

Powder Diffraction Pattern of 16TAC/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 crystals can be obtained by crystallization from solution and also by the method of mixing powdered samples in a mortar.

Molecular Structure of 16TAC/BNP Complex

The molecular structure and atomic numbering scheme for the complex is shown in Figure 3. The packing structure and crystal data of the complex are shown in Figure 4 and Table I, respectively. The asymmetric unit of 16TAC/BNP consists of one molecule of 16TAC, BNP, and water. The final fractional atomic coordi-

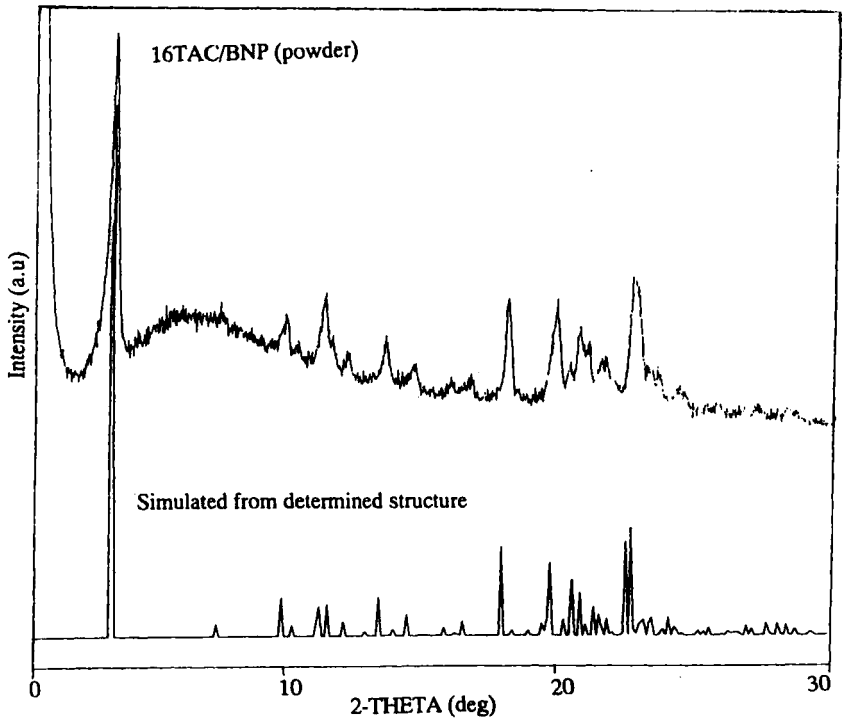

FIGURE 2 X-ray powder diffraction pattern of mixed powdered sample and simulated powder pattern of 16TAC/BNP

nates, 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.

Molecular Conformation of 16TAC/BNP

The dihedral angles in the alkyl chain part are in the range of 180±19° with the exception of C7-C8-C9-C10 [-64.5(9)°] and C16-C17-C18-C19 [67(3)°]. In Figure 3, it is observed that C18 has a larger temperature factor than other carbon atoms in the host and guest molecules. The bond distances and angles in the 16TAC molecule are normal and did not show any significant deviation from the values reported for 16TAC [1]. The bond distances and angles are in the range, from 1.50(1) to 1.530(6)Å for C-C, and from 110.8(3) to 116.4(8)° for C-C-C, and from 1.486(4) to 1.502(4)Å for N-C, and from 107.3(2) to 111.8(2)° for C-N-C. The average C-C bond length and C-C-C bond angle are 1.513(3)Å and

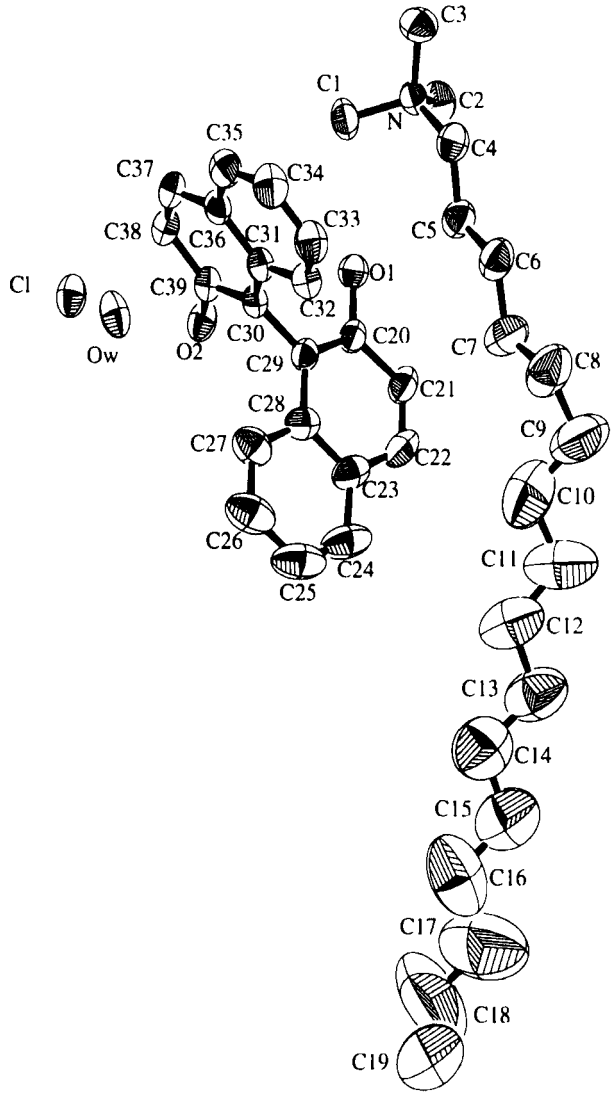

FIGURE 3 Molecular structure and atomic numbering of 16TAC/BNP. The 40% probability ellipsoids are shown. Hydrogen atoms are omitted for clarity of the structure

112.5(6)° respectively, whilst the average N-C bond length and C-N-C bond angle are 1.493(4)Å and 109.5(2)° respectively. In the naphthol moieties all the C-C, C-O bond lengths and C-C-C bond angles and C-C-C-C dihedral angles showed similar values found in (±)-1,1′-bi-2-naphthol [12,13]. The dihedral

angle between the two naphthol planes defined by O1, C20, ..., C29 and O2, C39, ..., C30 in BNP is 80.2(4)°. The mean deviations from the planarities of these naphthol moieties are 0.0293(4) and 0.0133(3)Å, respectively.

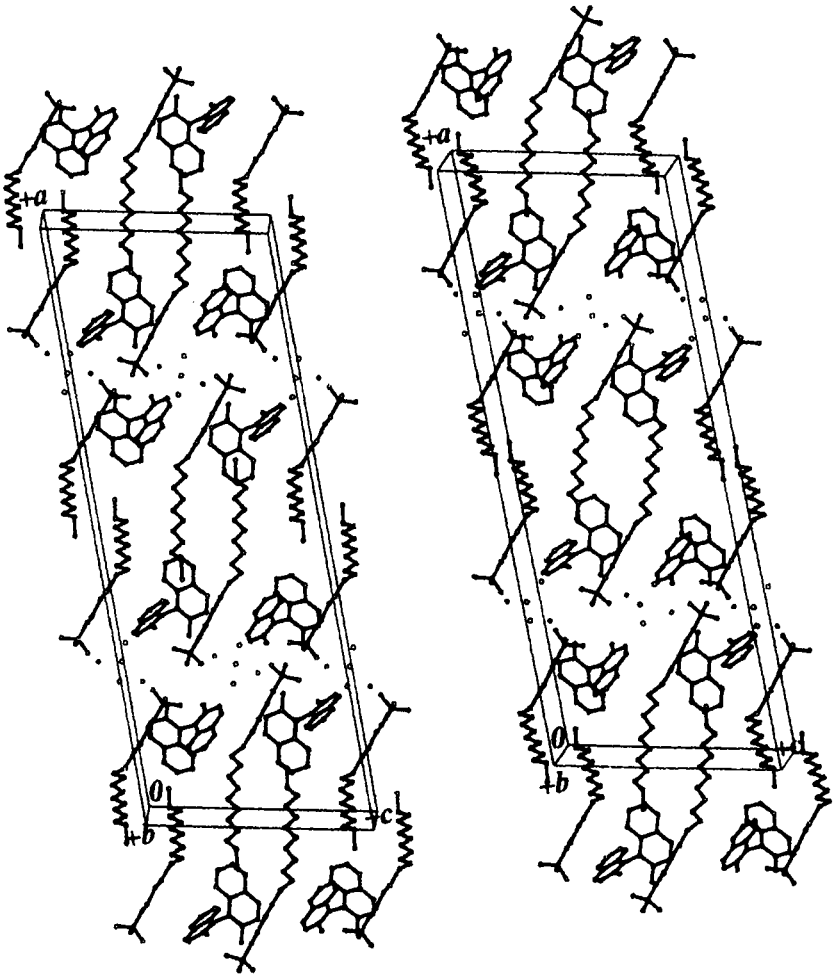

FIGURE 4 Stereo drawing of 16TAC/BNP viewed along the *b*-axis

Crystal Packing and Host-Guest Interactions in 16TAC/BNP

The crystal packing arrangement of 16TAC molecules with the naphthol moieties viewed along the *b*-axis is illustrated in Figure 5. The chloride anion partici-

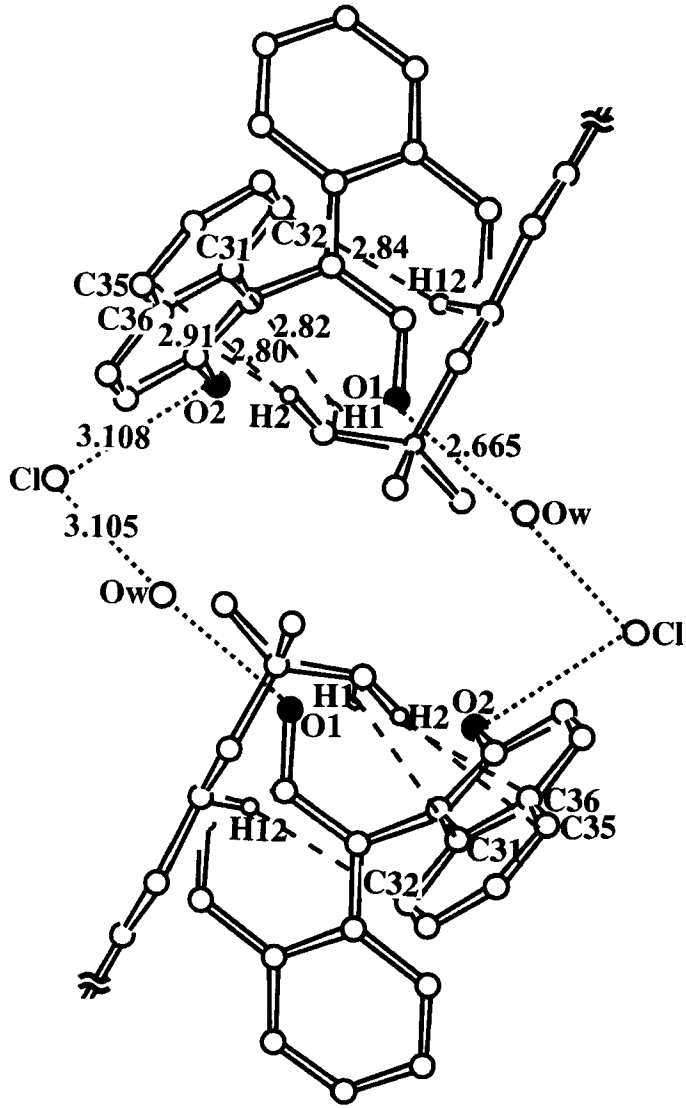

FIGURE 5 The C-H···π interactions, and hydrogen bonds observed in the 16TAC/BNP complex. The broken lines represent C-H···π interactions, whilst the dotted lines represent hydrogen bonds. The shaded circles denote oxygen atoms of BNP. Only part of the packing arrangement in Figure 4 is shown for clarity on interactions between the host and guest molecules

pates in a hydrogen bond with one of the OH groups of BNP (O2···Cl, 3.108(2)Å). A strong hydrogen bond was found between the other OH group of BNP and the oxygen of water molecule (O1···OW, 2.665(3)Å). The chloride

anion also plays an important role as the hydrogen acceptor of the OH group of water molecule (OW···Cl, 3.105(3)Å). There were also short C-H···C distances between a hydrogen atom (H12) of the alkyl chain together with the methyl group (C1), and carbon atoms of the naphthol ring with O2. This suggested an existence of C-H···π interactions. The atomic distances shorter than the sum of the van der Waals radii (2.97Å) [14] were C31···H1 2.82, C32···H12 2.84, C35···H2 2.80, and C36···H2 2.91Å. The short contacts between non-bonded carbon atoms with values less than that of the sum of van der Waals (3.54Å) [14] are C1···C31 3.417(5)Å, and C1···C36 3.363(5)Å. The hydrophobic long alkyl chain of the 16TAC molecule contributes to the unique molecular packing arrangement observed in the 16TAC/BNP complex. The alkyl chain is bent at C10 and does not exhibit the complete zig-zag planes of the alkyl chain as reported on 16TAC [1]. The alkyl chain which is bent beyond the midpoint is unique and different from the usual extended alkyl chain conformation in monoalkyltrimethylammonium halide salt complexes with aromatic organic guest molecules. The BNP molecules are completely trapped between the 16TAC molecules, and the interdigitated arrangement of the 16TAC molecules are clearly observed in the *ac* -plane.

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.

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