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The Molecular Complexes of Monoalkylammonium Bromide Salts with (R)-(+)-1,1'-Bi-2-Naphthol and Rac-1,1'-Bi-2-Naphthol

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The crystal structures of hexyltrimethylammonium bromide (6TAB) adduct of (R)-(+)-1,1'-bi-2-naphthol (RBNP) and decyltrimethylammonium bromide (10TAB) adduct of rac-1,1'-bi-2-naphthol (BNP) have been determined by the X-ray diffraction method. The molecules of the 6TAB/RBNP complex are held in their aggregates by O1···Br [3.228(4)Å], O2···Br [3.225(6)Å] intermolecular hydrogen bonds and C-H···π interactions between the alkyl chain, methyl groups and aromatic rings of the naphthol moieties. It was observed in the crystal structure of 10TAB adduct of BNP that the crystal structure formation was mainly stabilized by the intermolecular hydrogen bonds between the bromide anion and OH group of BNP (O1···Br1 [3.241(4)Å], O2···Br2 [3.172(3)Å]). In both complexes, the packing arrangement of the monoalkylammonium bromide salts with non-planar aromatic molecules are different from those observed in complexes of monoalkylammonium bromide salts with planar aromatic guest molecules. X-ray powder diffraction studies on both complexes showed that the crystals complex can be obtained by crystallization from solution and also by mixing powdered samples in a mortar. This study has shown that a non-chiral host amphiphile can form a complex with either a chiral or racemic aromatic guest compound.

Keywords: Decyltrimethylammonium bromide; Hexyltrimethylammonium bromide; Molecular complex; Crystal structure; Clathrate compound; Non-planar aromatic

INTRODUCTION

Organic supramolecular crystals have recently become an important subject of research, since they exhibit particular solid-state properties and behaviour which

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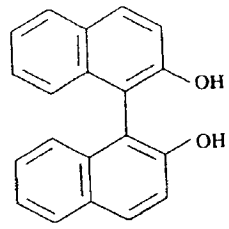
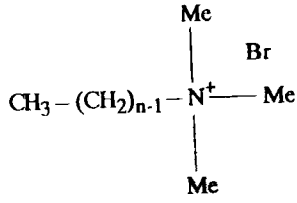
cannot be achieved in single-component crystals. For example, there have been extensive studies in hydrogen-bonded molecular complexes for molecular recognition [1], clathrate crystals for enantio-differentiation [2], charge-transfer complexes for molecular conductors [3]. Intermolecular (supramolecular) interactions are the foundation for highly specific biological processes such as the substrate binding by enzymes or receptors. The molecular aggregation between monoalkylammonium salts (synthetic surfactants) and organic molecules are of great importance in the mechanistic study of the role of membranes [4]. The amphiphilic molecules with long hydrophobic alkyl chains, such as phospholipids in biological membranes and synthetic surfactants do aggregate spontaneously in an aqueous solution. The molecular aggregations take various types of higher-order organisation, for example, as bimolecular layer arrangement, spherical micelles and rod-shaped micelles. Most of the amphiphilic molecules take very similar two-dimensional smectic layers in the solid state. The smectic layers stack along the normal direction to the layer surface to make a three-dimensional crystal structure. The chemical structure of an element amphiphile is a factor for the molecular arrangement in the smectic layer. 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 [5,6]. Meanwhile, in the cases of monoalkyltrimethylammonium salts, [7] alkyl chains from both sides of the layer surfaces are usually packed together in an interdigitating manner to compensate for the large hydrophilic head part.

It has recently been found that most monoalkylammonium salts have abilities to form complexes with planar aromatic compounds, and adopt a general molecular packing manner [7]. The formation of the complex can also be obtained by mixing both powdered samples of a monoalkylammonium salt and an aromatic compound in a mortar [7]. However, studies on molecular aggregation between monoalkylammonium salts with a chiral or racemic non-planar aromatic compound have not been reported yet. Thus, we were challenged to investigate how non-chiral monoalkylammonium salts can form clathrate complexes with racemic or chiral non-planar aromatic compounds. A series of monoalkylammonium bromide compounds with various lengths of hydrophobic alkyl chains were used in an attempt to obtain single crystals of their complex with (R)-(+)-1,1'-bi-2-naphthol (RBNP) or rac-1,1'-bi-2-naphthol (BNP).

In this paper, the crystal structures of hexyltrimethylammonium bromide (6TAB) adduct of RBNP and decyltrimethylammonium bromide (10TAB) adduct of BNP single crystal structures determined by the X-ray diffraction method will be discussed. In this manuscript the 6TAB and 10TAB are termed as *host* molecules whilst BNP and RBNP are termed as *guest* molecules.



(a)



(b)

FIGURE 1 Chemical structures of host amphiphile and guest aromatic molecule. (a) Guest aromatic molecule: (R)-(+)-1,1'-Bi-2-naphthol (RBNP), Rac-1,1'-Bi-2-naphthol (BNP) (b) Host amphiphiles: n = 6, Hexyltrimethylammonium bromide (6TAB) n = 10, Decyltrimethylammonium bromide (10TAB)

EXPERIMENTAL AND CRYSTAL STRUCTURE DETERMINATION

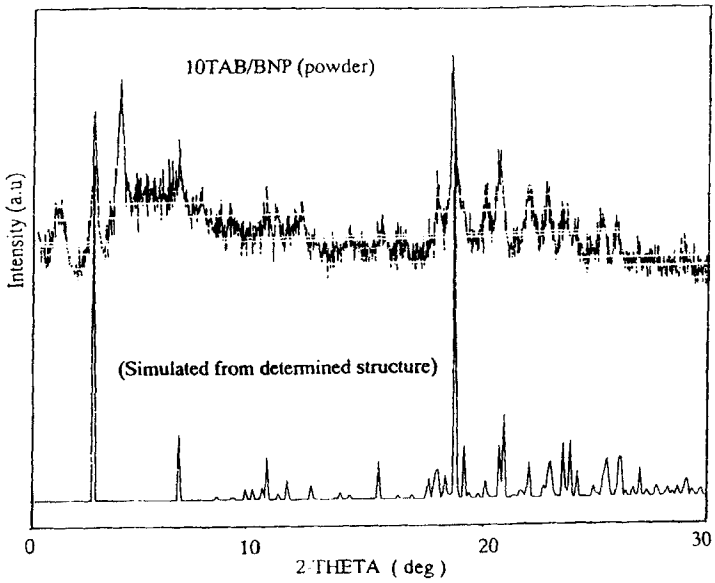
Preparation of Hexyltrimethylammonium Bromide Adduct of (R)-(+)-1, 1'-Bi-2-Naphthol and Decyltrimethylammonium Bromide Adduct of Rac-1, 1 '-Bi-2-Naphthol

The samples of (R)-(+)-1,1'-bi-2-naphthol (hereafter, RBNP), hexyltrimethylammonium bromide (6TAB) and decyltrimethylammonium bromide (10TAB) were 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.

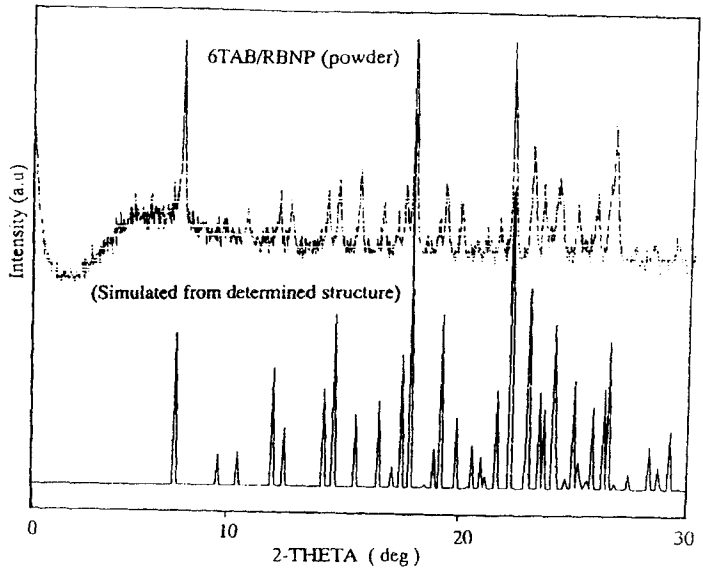
The 6TAB adduct of RBNP (6TAB/RBNP) was prepared by treating 6TAB with RBNP in the molar ratio of 1:1 in ethylacetate/acetone (2ml/8ml) solvent mixture. The mixture was simultaneously stirred and warmed at 30–40°C for 20mins in a 10ml glass bottle. The resulting warmed mixture was then covered with perforated plastic thin wrap and kept in an incubator at 20°C for 7–10 days to obtain colourless needle-like single crystals. Similarly, the 10TAB adduct of BNP (10TAB/BNP) was prepared by the same method to obtain colourless needle-like single crystals. The crystals obtained were removed from their viscous solutions and cleaned with diethylether and kept for X-ray diffraction studies.

X-Ray Powder Diffraction

The X-ray powder diffraction methods were used to identify the formation of the two crystal complexes. The X-ray diffraction of powdered samples of the



(a)



(b)

FIGURE 2 X-ray powder diffraction patterns of mixed powdered sample and simulated powder patterns of (a) 10TAB/BNP (b) 6TAB/RBNP

host/guest adducts were 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 patterns (Figure 2) for the powdered samples of the two adducts were compared with simulated powder patterns based on atomic coordinates of the respective single crystals determined in this study. This 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 for the adducts of 6TAB and 10TAB were carried out using a four-circle diffractometer (Rigaku AFC5R) fitted with graphite monochromatized CuKα radiation (λ = 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 $79.13<2\theta<79.98°$ for the 6TAB adduct and 25 reflections in the range of $76.51<2\theta<79.43°$ for the 10TAB adduct. The intensity data for 6TAB and 10TAB adducts were collected at 298K in the ω-2θ scan mode with a scanning speed of 8°/min and scanning widths of $\Delta w = (1.21 + 0.30 \tan\theta)°$ and $\Delta w = (1.68 + 0.30 \tan\theta)°$ respectively. Three reference reflections were measured after every 100 reflections. In both cases, significant intensity decreases were observed (1.87% decrease in 6TAB/RBNP and 0.75% decrease in 10TAB/BNP). Decay correction was applied to the intensity data of both complexes. An empirical absorption correction based on azimuthal scans of several reflections was also applied in the two data. The data were also corrected for Lorentz and polarization effects. The parameters for data collection and crystal data for the 6TAB and 10TAB adducts are summarized in Table I.

Determination and Refinement of the Crystal Structures

The crystal structures of 6TAB and 10TAB adducts were solved by direct methods (SIR92) [9] and expanded using Fourier techniques (DIRDIF94) [10]. The non-hydrogen atoms of 6TAB and 10TAB adducts were refined anisotropically. Since the hydrogen atoms attached to O(1) and 0(2) of the 6TAB adduct could not find its position in the difference Fourier map, they were not included in the calculation. In the 10TAB adduct case, the positions of hydrogen atoms attached to O(1) and O(2) were found in the difference map and refined isotropically. All the other hydrogen atoms of both adducts were introduced by geometrical calculations but not refined.

TABLE I Crystal data and data collection parameters for the 6TAB/RBNP and 10TAB/BNP complexes

	6TAB/RBNP	*10TAB/BNP*
Molecular Formular	$C_9H_{22}N^+Br^-{\cdot}C_{20}H_{14}O_2$	$2C_{13}H_{30}N^+Br^-{\cdot}C_{20}H_{14}O_2$
Formular Weight	510.51	846.91
Space group	$P2_1$	$P2/a$
a/Å	9.2350(9)	19.260(2)
b/Å	12.243(1)	10.001(3)
c/Å	11.5242(8)	25.111(1)
α/°	90	90
β/°	92.399(6)	101.215(5)
γ/°	90	90
Volume /Å^3	1301.8(2)	4744(1)
Z	2	4
Dcalc/g cm^{-3}	1.302	1.186
Dobs/g cm^{-3}	1.30	–
F(000)	536	1800
Crystal dimensions /mm	0.1 × 0.2 × 0.2	0.20 × 0.15 × 0.20
h,k,l range	0–10, 0–14, −13-13	0–22, 0–6, −28-28
μ(CuKα) /cm^{-1}	23.39	24.25
Maximum 2θ /°	120	120
No. of Observed Reflections	Total: 2183	Total:6078
	Unique: 2045	Unique:5919
No. of Reflections for R	1730 (I>1.00σ(I))	4044 (I>2.00σ(I))

Bond lengths in the 6TAB molecule were restrained during refinement calculations. All C-C bonds were restrained to 1.520Å with weight 0.001, three of the four N-C bonds to 1.470Å with weight 0.001, and one attached to the methylene group to 1.470Å with weight 0.0005. The atomic distances between C4···C6, C6···C8, C5···C7, C7···C9 and C1···C4, C2···C4, C3···C4 were restrained to 2.520Å with weight 0.001 to maintain appropriate values for bond angles in the host molecule. In the case of the 10TAB adduct, all the C-C bonds were restrained to 1.520Å with weight 0.001 and all the C-N bonds restrained to 1.470Å with weight 0.001 but no restraining conditions for bond angles were applied. The final cycles of full-matrix least-squares refinement of 6TAB/RBNP were based on 1730 reflections, 298 variable parameters and 19 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 = 0.055 and Rw = 0.090 respectively. The maximum and

minimum peaks on the final difference Fourier map corresponded to 0.48 and $-0.36e^-/Å^3$ respectively. The final cycles of full-matrix least-squares refinement of 10TAB/BNP were based on 4044 reflections, 477 variable parameters and 26 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 $R = 0.046$ and $Rw = 0.069$ for all the non-hydrogen atoms and hydrogen atoms. The maximum and minimum peaks on the final difference Fourier map was 0.32 and $-0.38e^-/Å^3$. 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]. In both crystal structures solution neutral atom scattering factors were taken from Cromer and Waber [11].

RESULTS AND DISCUSSION

Powder Diffraction Patterns of 6TAB/RBNP and 10TAB/BNP Complexes

Most of the strong peaks in the powder diffraction patterns (Figure 2) correspond to the peaks in the simulated diffraction patterns, which suggest that both complex crystals can be obtained by crystallization from solution and also by the method of mixing powdered samples in a mortar.

Molecular Structure of 6TAB/RBNP and 10TAB/BNP Complexes

The molecular structure and atomic numbering scheme for the complexes are shown in Figures 3 (a) and (b). The packing structures and crystal data of the two complexes are shown in Figures 4 (a) and (b), and Table I respectively. The host/guest ratio of the 6TAB/RBNP complex is 1:1, whilst that of the 10TAB/BNP complex is 2:1. The bromide anion plays the role of a hydrogen acceptor of OH (O-H···Br) of BNP or RBNP to form intermolecular hydrogen bonds in both complexes. The final fractional atomic coordinates, anisotropic thermal parameters, bond lengths and angles and tables of observed and calculated structure factors for both complexes have been deposited at the Cambridge Crystallographic Data center, 12 Union Road, Cambridge, CB2 1EZ,UK.

Molecular Conformation of 6TAB/RBNP

The dihedral angles in the alkyl chain part are in the range of 180±10° with the exception of C6-C7-C8-C9 [80(1)°]. In Figure 3(a), it is observed that C6 has a

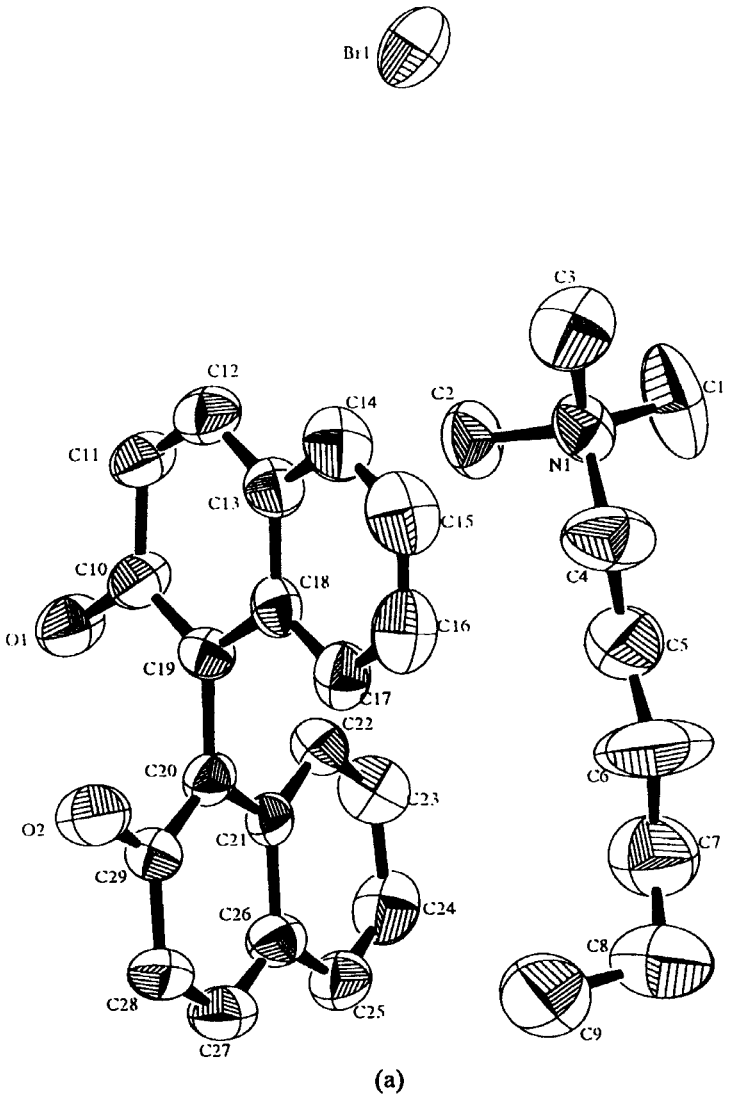
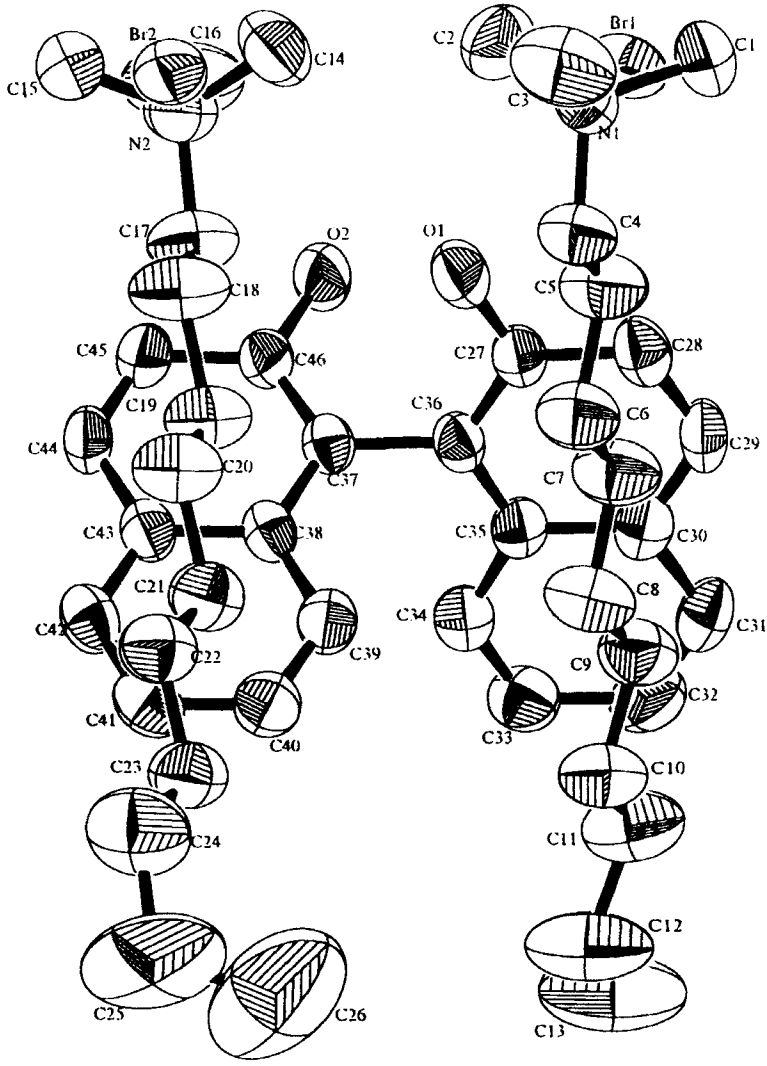


FIGURE 3 Molecular structure and atomic numbering of (a) 6TAB/RBNP. The 50% probability ellipsoids are shown. Hydrogen atoms are omitted for clarity of the structure

slightly larger temperature factor than other carbon atoms in the host and guest molecules. The bond distances and angles of the 6TAB molecule are in the range, from 1.499(6) to 1.524(6)Å for C-C, and from 111.5(6) to 113.0(6)° for C-C-C, and from 1.497(3) to 1.514(5)Å for N-C, and from 103.2(6) to 111.8(4)° for



(b)

FIGURE 3 Molecular structure and atomic numbering of (b) 10TAB/BNP. The 50% probability ellipsoids are shown. Hydrogen atoms are omitted for clarity of the structure

C-N-C. The average C-C bond length and C-C-C bond angle are 1.514(6)Å and 112.3(6)° respectively, whilst the average N-C bond length and C-N-C bond angle are 1.509(5)Å and 109.4(5)° 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,C10,.....,C19 and O2,C29,.....,C20 in RBNP is 72.3(8)°. The mean deviations from the planarities of these naphthol moieties are 0.0356(7) and 0.0303(6)Å respectively.

Crystal Packing and Host-Guest Interactions in 6TAB/RBNP

The crystal packing arrangement of 6TAB molecules with the naphthol moieties viewed along the *b*-axis is illustrated in Figure 5. The bromide anion participates in an intermolecular hydrogen bond network (Figure 5) with both OH groups of RBNP (O1···Br, O2···Br) with distances of 3.228(4)Å and 3.225(6)Å respectively. Interestingly, many C-H···C distances between hydrogen atoms of the alkyl chain, methyl groups and carbon atoms of the aromatic rings suggested C-H···π interactions. Only the atomic distances shorter than the sum of the van der Waals radius (2.97Å) were shown in Figure 5. The short contacts between the non-bonded carbon atoms, carbon atom and oxygen atoms less than 3.60Å are C1···C10 3.57(1), C2···C12 3.54(1), C2···C13 3.476(9), C8···C12 3.51(1), C3···O1 2.797(8), C3···O2 3.46(1)Å, and C2···O2 3.49(1)Å.

The arrangement of 6TAB molecules in Figure 5 are not similar to the common molecular packing structural pattern observed in most of the structures reported on monoalkylammonium salts with planar aromatic molecules [7]. A 2_1 symmetry at (u = 0.0, w = 0.0) makes a one-dimensional stacking of naphthol moiety (Figure 5) along the *b*-axis, whilst naphthol moieties related by the 2_1 symmetry at (u = 0.5, w = 0.5) are sandwiched between 6TAB molecules also related by this symmetry.

Molecular Conformation of 10TAB/BNP

The crystal structure analysis of the 10TAB/BNP complex revealed that the alkyl chains in the two 10TAB molecules have *trans* conformation with one exception of *gauche* conformation for C23-C24-C25-C26[59(1)°] with C26 out of the zigzag plane. The other dihedral angles in the two alkyl chains are in the range of 180±10°. The bond distances and angles of the 10TAB molecule in N1 chain are in the range, from 112.8(5) to 117.2(5)° for C-C-C, and from 1.488(7) to 1.512(7) Å for C-C, and from 1.475(6) to 1.502(5)Å for N1-C and from 107.6(5) to 111.7(4)° for C-N1-C. The average C-C bond length and C-C-C bond angle are 1.501(6)Å and 114.8(5)° respectively. The average N1-C bond length and C-N1-C bond angle are 1.49(6)Å and 109.5(5)° respectively. In N2 chain, the bond distances and angles are in the range, from 1.484(8) to 1.520(6)Å for C-C, and from 1.483(6) to 1.496(5)Å for N2-C, and from 112.3(5) to 114.0(5)° for C-C-C, and from 107.0(5) to 111.6(4)° for C-N2-C. The average C-C bond

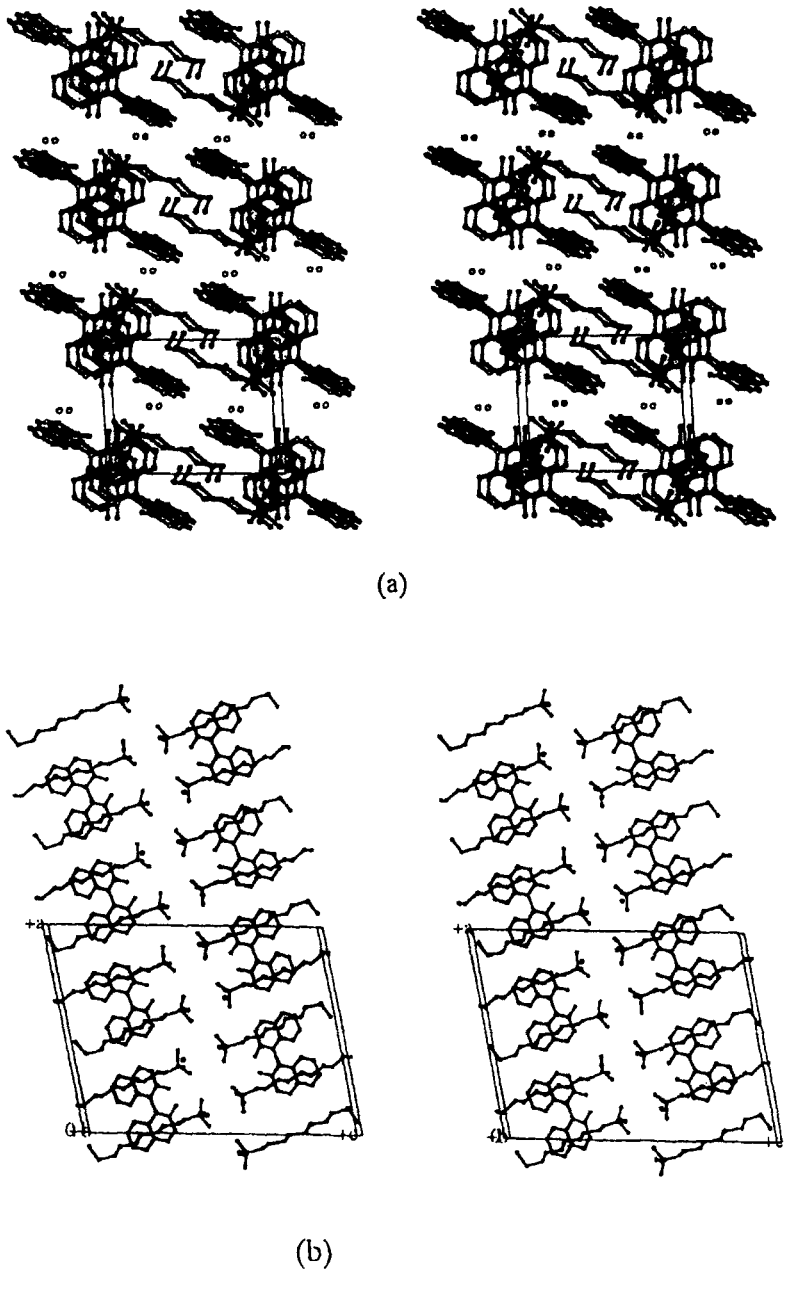


FIGURE 4 Stereoscopic views of (a) 6TAB/RBNP (b) 10TAB/BNP along the *b*-axis

length and C-C-C bond angle are 1.501(6)Å and 114.8(5)° respectively The average N2-C bond length and C-N2-C bond angle are 1.489(6)Å and 109.5(5)° respectively. In both alkyl chains, larger temperature factors of the terminal carbon atoms were observed when compared with those of the other atoms in the host and guest molecules. The dihedral angle between the two naphthol planes defined by O1,C27,C28,...,C36 and O2,C46,C37,...,C45 is 69.6(1)°. The C-C, C-O bond lengths, C-C-C bond angles and C-C-C-C dihedral angles are very similar to those observed in (±)-1,1'-bi-2-naphthol [12,13]. The mean deviation from the planarities of these naphthol moieties in BNP are 0.0211(5) and 0.0212(5)Å respectively.

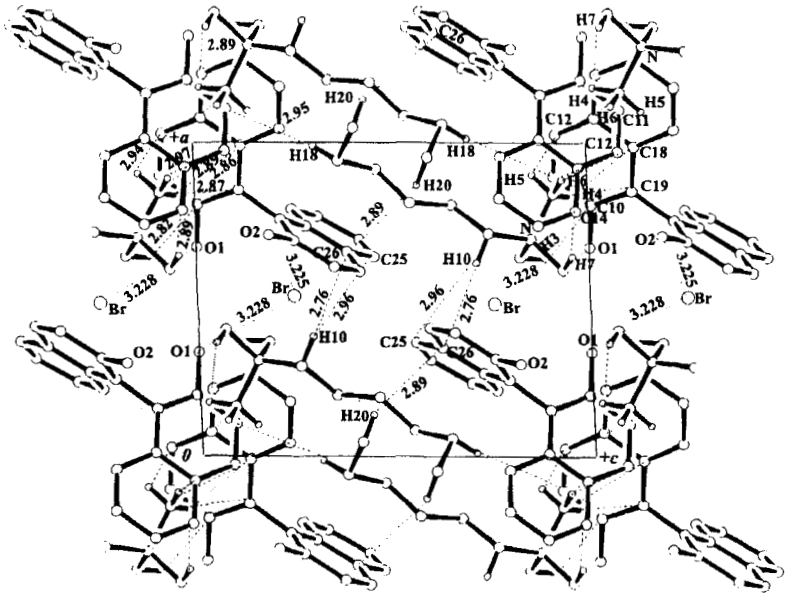


FIGURE 5 The C-H···π interactions, and hydrogen bonds observed in the 6TAB/RBNP complex. The broken lines represent C-H···π interactions, whilst the dotted lines represent hydrogen bonds

Crystal Packing and Host-Guest Interactions in 10TAB/BNP

The crystal structure of 10TAB/BNP was mainly stabilized by the intermolecular hydrogen bonding (Figure 4b) between the bromide anions and OH group of BNP (O1···Br1[3.241(4)Å], and O2···Br2[3.172(3)Å]). There was no short interaction less than the sum of van der Waals radii between host and guest molecules. The short contacts between non-bonded carbon atoms and oxygen atoms less than 3.60Å are C3···O2 3.600(8), C4···O2 3.353(7), C(29)···C(42) 3.470(7), and C17···O1 3.514(6)Å. The packing arrangement of 10TAB is also not similar

to the common structural pattern observed in complexes of monoalkylammonium bromide salts with planar aromatic molecules [7]. The alkyl chain planes of 10TAB molecules lie parallel to each of the naphthol planes in the *ac*-plane (Figure 4b).

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References

[1] J.M. Lehn, Angew.Chem.Int.Ed.Engl., **29**, 1304 (1990).
[2] G.Kaupp, Angew.Chem.Int.Ed., Engl., **33**, 728 (1994).
[3] J.R. Ferraro and J.M. Williams, Introduction to Synthetic Electrical Conductors, Academic Press, San Diego, 1987.
[4] T. Kunitake, Y. Okahata, J.Am.Chem.Soc., **99**, 3860 (1977).
[5] K. Okuyama, Y. Soboi, N. Iijima, K.Hirabayashi, T. Kunitake and T. Kajiyama, Bull.Chem.Soc.Jpn., **61**, 1485 (1988).
[6] K. Okuyama, N. Iijima, K.Hirabayashi, T.Kunitake and M. Kusunoki, Bull.Chem.Soc. Jpn., **61**, 2337 (1988).
[7] K. Okuyama,T. Ishii, K. Vongbupnimit and K. Noguchi, Mol. Cryst. Liq. Cryst., **312**, 185 (1996).
[8] TeXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).
[9] A. Altomore, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, **27**, 435(1994):SIR92.
[10] 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.
[11] D.T. Cromer, J.T. Waber, "International Tables for X-ray Crystallography", **Vol.IV**, The Kynoch Press, Birmingham, England, Table II.2A (1974).
[12] K. Mori, Y. Masuda, S. Kashino., Acta Crystallogr., Sect C (Cr.Str.Comm)., **49**, 1224 (1993).
[13] F. Toda, K. Tanaka, H. Miyamoto, H. Koshima, I. Miyahara, K. Hirotsu, J.Chem.Soc., Perkin Trans. **2**, 1877(1997).