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The crystal and molecular structure of 2:1 complex of the tetradecyltrimethylammonium bromide with rac-1,1′-bi-2-naphthol (14TAB/BNP) is reported. The 14TAB/BNP complex crystallizes in monoclinic space group C2/c. The asymmetric unit of the complex consists of two crystallographically independent molecules of 14TAB and one crystallographically independent molecule of BNP. The crystal structure of the complex is stabilized by mainly the intermolecular hydrogen bonding between the bromide anions and OH groups of BNP. The molecules are held in their aggregates by Ol ··· Br2, 3.220(4) Å and O2 ··· Br1, 3.161 (4) Å hydrogen bonding. The crystal-structure studies revealed that one of the alkyl chains has an all trans conformation, whereas the second alkyl chain does not have all trans conformation but has at least a gauche conformation. The packing structure is unique and different from those observed in complexes of monoalkyltrimethylammonium halides with planar aromatic molecules as well as those of 1:1 complexes of monoalkyltrimethylammonium halides with nonplanar aromatic molecules. The manner in which the 14TAB molecules lay parallel to the naphthol moieties are similar to that observed in 2:1 complex of 10TAB/BNP.

Keywords: crystal engineering; crystal structure; molecular interactions; molecular recognition; monoalkylammonium halides; surfactants

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INTRODUCTION

In the past years, synthetic lipids such as monoalkyltrimethylammonium halides (hereafter, host molecules) have been found to form inclusion complexes with planar aromatic molecules (hereafter, guest molecules) [1–5]. The complexes formed do so through the molecular-recognition phenomenon. These complexes are generally found to adopt packing patterns in which the guest molecules are sandwiched between two alkyl chains of the host molecules or trapped between the head and tail parts of host molecules, and also an arrangement in which the guest molecule lay either perpendicular or parallel to the alkyl chains [6]. However, with regard to research studies on packing patterns or modes of host and guest molecules in complexes of monoalkyltrimethylammonium halides with nonplanar aromatic molecules, none had ever been reported until recently [7–9] when we reported on (1) 1:1 inclusion complexes of monoalkyltrimethylammonium halides [that is, hexyltrimethylammonium bromide (hereafter, 6TAB), dodecyltrimethylammonium bromide (hereafter, 12TAB), dodecyltrimethylammonium chloride, (hereafter, 12TAC), tetradecyltrimethyl ammonium chloride (hereafter, 14TAC), hexadecyltrimethylammonium bromide (hereafter, 16TAB), hexadecyltrimethyl ammonium chloride (hereafter, 16TAC)] with rac-1,1′-bi-2-naphthol (hereafter, BNP); and (2) 2:1 complexes of decyltrimethylammonium bromide (hereafter, 10TAB) with BNP (hereafter, 10TAB/BNP) [9]. In our research studies, the BNP molecule was chosen by virtue of its nonplanar shape and also as a good candidate for probable future studies on resolution of racemic compound by a nonchiral surfactant molecule. The purpose of this research study is to know the general packing pattern as well as intermolecular interactions in 2:1 complexes of monoalkyltrimethylammonium halides with BNP and compare these with those of 1:1 complexes of monoalkyltrimethylammonium halides with BNP, because the knowledge on the packing pattern and intermolecular interactions in these complexes may be useful or may be utilized in the future to design a probable supramolecular system suitable for separation processes, such as the isolation of nonplanar aromatic molecules or resolution of racemic mixtures using nonchiral surfactant molecules. Presently, there is no report on the resolution of racemic mixtures using nonchiral molecules, and such a study demonstrates an inexpensive method of resolving racemic mixtures or racemic drugs in chemical or pharmaceutical industries.

The studies on the reported complexes revealed that the 1:1 complexes of monoalkyltrimethylammonium halides with the nonplanar aromatic molecules (BNP) adopt a packing pattern in which the

BNP molecule (hereafter, guest) is sandwiched between two alkyl chains of the host molecules as observed in 1:1 inclusion complexes of monoalkyltrimethylammonium halides with planar aromatic molecules. However, in the case of 2:1 complex of decyltrimethylammonium bromide (hereafter, 10TAB) with BNP [9], the packing pattern is different from those of 1:1 inclusion complexes of monoalkyltrimethylammonium halides with nonplanar aromatic molecules, as well as those of 1:1 and 2:1 inclusion complexes of monoalkyltrimethylammonium halides with planar aromatic molecules [6]. It was also observed that the alkyl chains in the 1:1 complexes are bent, whereas in the 2:1 complex of 10TAB with BNP, the alkyl chains are not. The hydrogen bonding and $C-H \cdots \pi$ interactions are the driving forces behind molecular recognition scheme in the 1:1 complexes, whereas in the 2:1 complex of 10TAB/BNP, the molecular aggregation is controlled mainly by hydrogen bonds.

Thus, in respect to the reports on our previous extensive work on the 1:1 complexes of monoalkyltrimethylammonium halides with BNP, and that of 2:1 complex of 10TAB/BNP, we reported on the 2:1 complex of the tetradecyltrimethylammonium bromide (hereafter, 14TAB) with BNP (hereafter, 14TAB/BNP), because our investigations presently are focused on knowing the general packing pattern and intermolecular interactions in the series of 2:1 complexes of both short and long alkyl chain substituted monoalkyltrimethylammonium bromides with BNP. In this regard, the packing pattern and the intermolecular interactions in the crystal structure of the 2:1 complex of 14TAB/BNP are reported in this manuscript.

EXPERIMENTAL METHODS AND CRYSTAL STRUCTURE DETERMINATION

Preparation of 14TAB/BNP Complex

The 14TAB (hereafter, host) was purchased from Tokyo Chemical Industry Company Ltd, whereas the BNP (hereafter, guest) was purchased from Wako Chemical Industry Ltd. Tokyo, Japan. Several attempts to employing probable solvents such as ethylacetate, acetone, and ethanol to obtain suitable crystals of 14TAB adduct of BNP (14TAB/BNP) were unsuccessful. However, by adopting the solvent-mixture method, we successfully obtained crystal complex of 14TAB/BNP by treating 14TAB with BNP in the molar ratio of 1:1 in a suitable solvent mixture of ethylacetate/acetone (2 ml/8 ml). The mixture was simultaneously stirred and warmed at 303–313 K for 20 min in a glass bottle. The resulting warmed mixture was then

covered with perforated plastic thin wrap and kept in an incubator at 293 K for 7–10 days to obtain colorless needle-like single crystals.

X-Ray Intensity Data Collection

The determination of the unit cell dimensions and collection of the X-ray intensity data for the complex 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 least-squares refinement using the setting angles of 25 carefully centered reflections in the range of $60 < 2\theta < 62^\circ$. The intensity data for the adduct were collected at 298 K in the ω-2θ scan mode with a scanning speed of 8°/min and scanning widths of $\Delta w = (1.84 + 0.30 \tan\theta)^\circ$. Three reference reflections were measured after every 150 reflections. 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 intensity collection and crystal data for the complex 14TAB/BNP are shown in Table 1.

Determination and Refinement of the Crystal Structure

The crystal structure of the complex was solved by direct methods (SIR92) [10] and expanded using Fourier techniques (DIRDIF94) [11]. The nonhydrogen atoms of the 14TAB molecules were refined anisotropically. Because the hydrogen atoms attached to O(1) and O(2) of 14TAB/BNP complex could not find their position in the difference Fourier map, they were not included in the calculation. All the other hydrogen atoms of the complex were introduced by geometrical calculations but not refined.

The C–C and N–C bonds in the 14TAB molecule were restrained to 1.520 and 1.490 Å with weight 0.0005 during refinement calculations to maintain appropriate values for bond lengths. The final cycles of full-matrix least-squares refinement were based on 4857 reflections, 541 variable parameters, and 51 geometrical restraints. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$, where $w = 1/\sigma^2(Fo)$. The final R-values are $R = 0.086$ and $Rw = 0.100$. The maximum and minimum peaks on the final difference Fourier map was 0.75 and -0.75 e Å^{-3}. All the calculations performed during data processing and crystal structure analysis were done using the teXsan software package for crystal structure analysis from the Molecular Structure Corporation [12]. Neutral atom scattering factors were taken from Cromer and Waber [13]. The final atomic coordinates and anisotropic thermal

TABLE 1 Crystal Data and Data Collection Details for 10TAB/BNP [9] and 14TAB/BNP Complexes

Complex	10TAB/BNP [9]	14TAB/BNP
Molecular formula	$C_{46}H_{74}O_2N_2Br_2$	$C_{54}H_{90}O_2N_2Br_2$
Crystal system	Monoclinic	Monoclinic
Formula weight	846.91	959.13
Space group	$P2/a$	$C2/c$
a/Å	19.260(2)	60.000(1)
b/Å	10.001(3)	9.988(3)
c/Å	25.111(1)	19.145(3)
$\alpha/^\circ$	90	90
$\beta/^\circ$	101.215(5)	101.720(1)
$\gamma/^\circ$	90	90
Volume/Å^3	4744(1)	11234(4)
Z	4	8
D_{calc}/g cm^{-3}	1.137	1.134
F(000)	1800	4112
Crystal dimensions/mm	$0.20 \times 0.15 \times 0.20$	$0.20 \times 0.20 \times 0.20$
μ(CuKα)/cm^{-1}	24.25	21.00
Maximum $2\theta/^\circ$	120	120
No. of reflections measured	Total: 6078 Unique: 5919	Total: 9012 Unique: 8914
No. of reflections for R	4044 [$I > 2.00\sigma(I)$]	4857 [$I > 1.00\sigma(I)$]
R-factor	0.046	0.088
Rw	0.069	0.103
Goodness of fit	1.41	1.33
Absorption correction		
Minimum transmission (%)	82.00	65.6
Maximum transmission (%)	100	100

parameters, torsional angles, bond lengths, and bond angles for the complexes have been deposited at the Cambridge Crystallographic Data Centre (CCDC), reference number CDDC 160239.

RESULTS AND DISCUSSION

Molecular Structure of 14TAB/BNP Complex

The molecular structure and atomic numbering scheme for the complex is shown in Figure 1. The asymmetric unit consists of two crystallographically independent molecules of 14TAB and one crystallographically independent molecule of BNP. The host–guest ratio is 2:1. The bond distances and angles of the 14TAB molecule in the N1 chain are in the range from 111.7(4) to 113.5(4)° for C−C−C, from

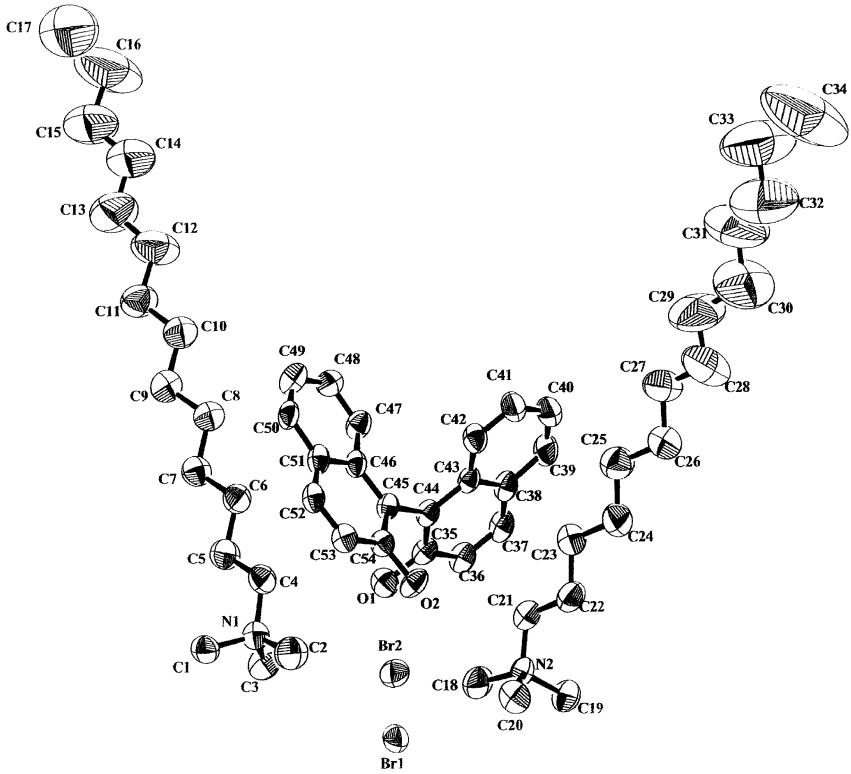


FIGURE 1 Molecular structure and atomic numbering of 14TAB/BNP. The 40% probability ellipsoids are shown. Hydrogen bonds are omitted for clarity of the structure.

1.508(4) to 1.523(5) Å for C–C, from 1.489(8) to 1.506(9) Å for N1–C, and from 107.3(5) to 112.3(5)° for C–N1–C. The average C–C bond length and C–C–C bond angle are 1.517(4) Å and 112.4(4)°, respectively. The average N1–C bond length and C–N1–C bond angle are 1.496(7) Å and 109.5(5)°, respectively. In the N2 chain, the bond distances and angles are in the range from 1.508(4) to 1.524(5) Å for C–C, from 1.487(4) to 1.502(8) Å for N2–C, from 111.6(4) to 113.2(4) for C–C–C, and from 106.8(5) to 112.8(5)° for C–N2–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 N2–C bond length and C–N2–C bond angle are 1.497(5) Å and 109.5(5)°, respectively.

The alkyl chain attached to the N1 atom has an *all trans* conformation, whereas the alkyl chain attached to N2 does not have *all trans*

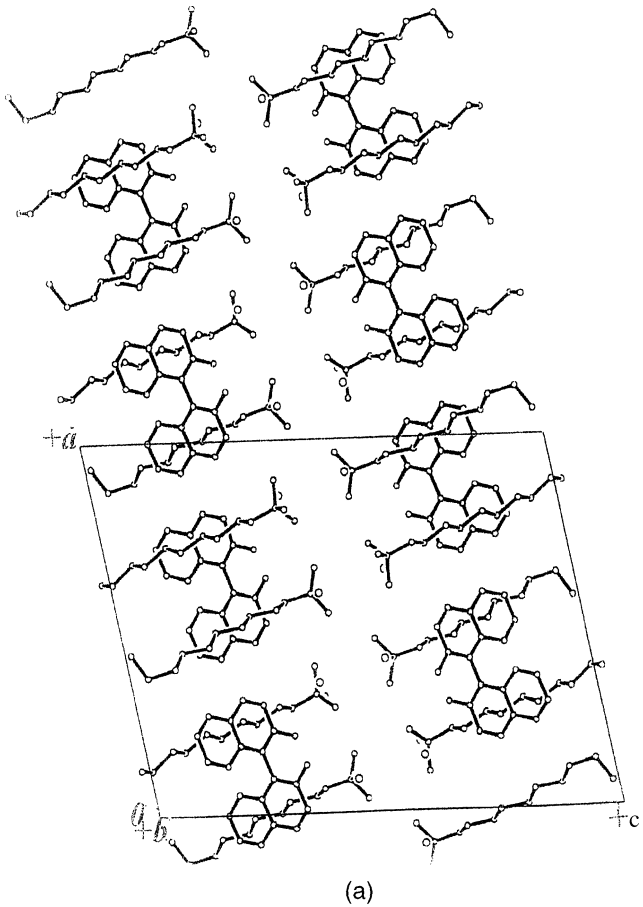


FIGURE 2 The crystal structure of 2:1 complexes of (a) 10TAB/BNP [7] and (b) 14TAB/BNP.

conformation but has a *gauche* conformation about C32-C33 [57(6)°]. The torsional angles in the two alkyl chains are in the range of $180 \pm 49°$. The temperature factors of the atoms in the BNP and 14TAB molecules are generally reasonable. Within the benzene rings of the naphthol moiety (1) and naphthol moiety (2), the torsional angles about C−C bonds are close to 0 or 180° and exhibit the planarity in the aromatic rings. The mean deviation from plane in naphthol plane (1) and naphthol plane (2) are both 0.0266 Å. The dihedral angle between the two naphthol planes defined by O1, C35 ··· C44 and O2, C54 ··· C45 in BNP is 68.01(6)°. The sum of the bond angles in the

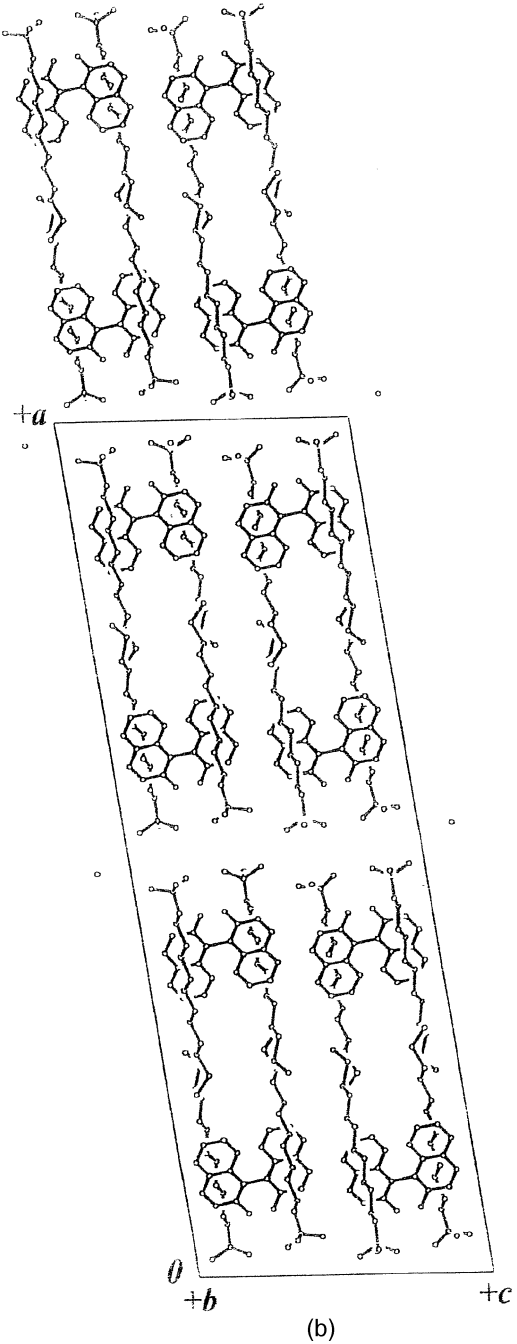
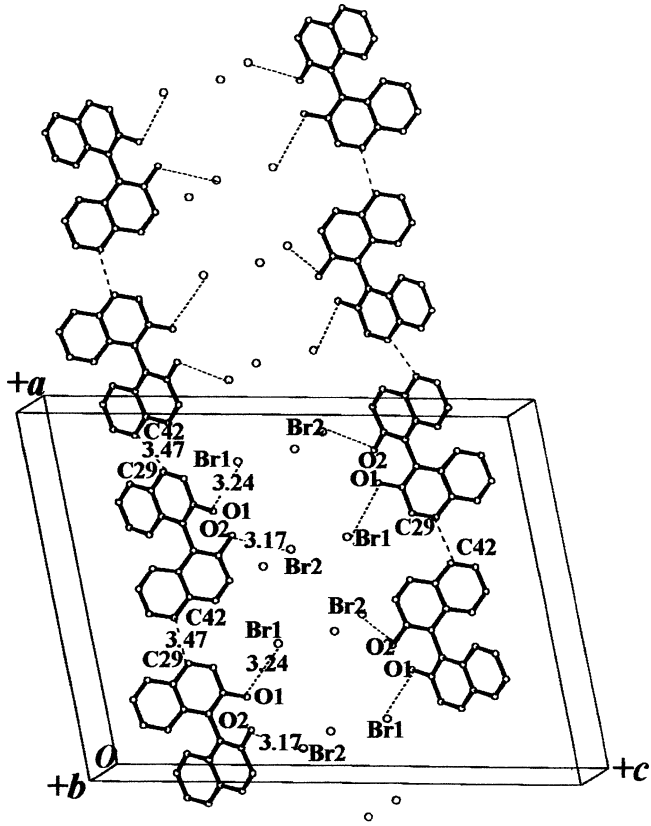


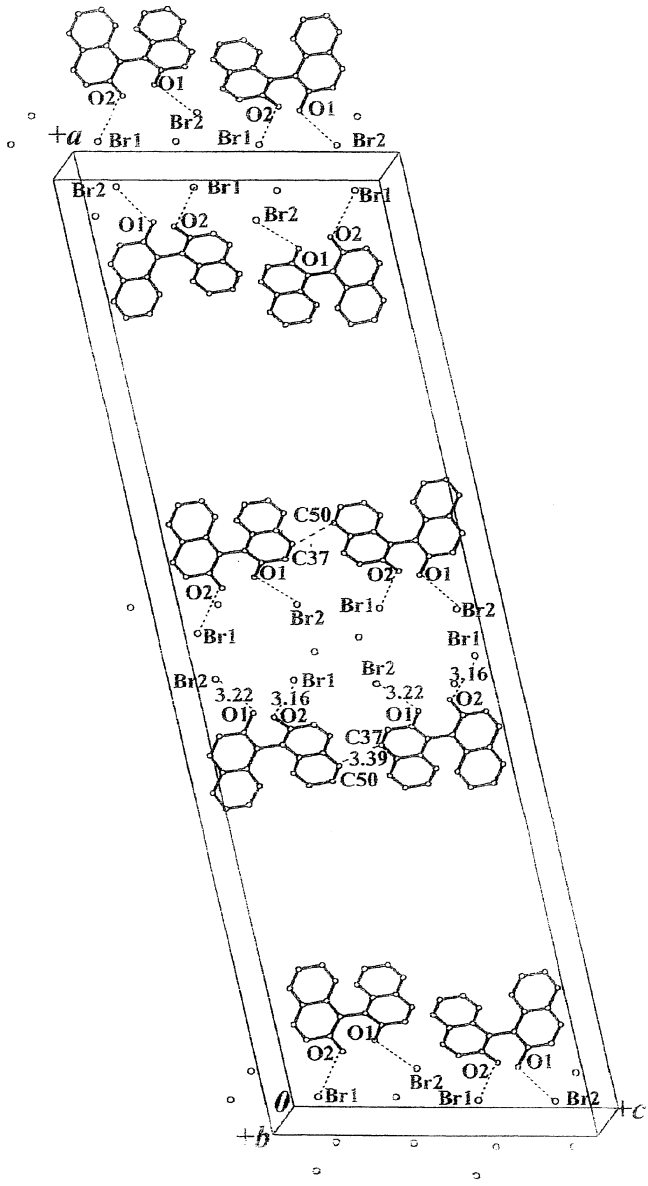
FIGURE 2 Continued.



(a)

FIGURE 3 The hydrogen bonds and C ··· C short contacts observed in (a) 10TAB/BNP and (b) 14TAB/BNP. The dotted lines represent hydrogen bonds, whereas the broken lines represent C ··· C short contacts. The host molecule (14TAB) are omitted for clarity of the intermolecular contacts.

benzene rings of the naphthol groups are equal to 720°, and those of the angles about C-atoms are equal to 360°. This suggests that the benzene rings do not deviate from the regular hexagon shape. The C−C bond connecting two naphthol rings is a length of 1.498(7) and is not significantly longer than the corresponding *cisoid* racemate conformation (1.475 Å) [14]. The bond lengths and angles in the naphthalene rings show typical conjugated double-bond character. The average value of C−C bond length and C−C−C bond angles in naphthalene ring (1) are 1.393(8) Å and 120.2(6)°, whereas in naphthalene



(b)

FIGURE 3 Continued.

(2), the values are 1.392(8) Å and 120.5(5)°, respectively. The values in the two naphthalene rings do not differ significantly from each other and show aromatic rings without any deformation. The deviations of the naphthol hydroxyl oxygen atoms from each plane of the naphthalene rings (1) and (2) are 0.0338 Å and −0.0384 Å, respectively, and do not significantly differ from each other. This implies that the orientation of the oxygen atoms in the naphthalene rings have good planarity. The O−C bond lengths are 1.369(7) and 1.361(7) Å for O1-C35 and O2-C54, respectively, and the average value of 1.365(7) Å is not significantly different from the usual value for C−O bond length [1.36(2) Å] [15] in phenols.

Packing Structure and Molecular Interactions in 10TAB/BNP and 14TAB/BNP

The crystal-packing structure of the 10TAB/BNP [9] and 14TAB/BNP complexes viewed along the *b*-axis are shown in Figure 2. Both crystal complexes crystallize in monoclinic crystal system (Table 1). The packing structure in the 2:1 nTAB/BNP (where n = 10, 14) crystal complexes are unique and different from the 1:1 complexes of both short and long alkyl chain substituted monoalkyltrimethylammonium halides with BNP as well as those of 1:1 and 2:1 complexes of monoalkyltrimethylammonium salts with planar aromatic molecules [1–5]. The manner in which the 14TAB molecules lay parallel to the naphthol moieties are similar to that observed in 2:1 complex of 10TAB/BNP [9] (Fig. 2a).

The crystal structures of both complexes are stabilized by mainly the intermolecular hydrogen bonding between the bromide anions and OH groups of BNP (Fig. 3). These are (O1 ··· Br1, 3.241(4) Å and O2 ··· Br2 [3.172(3) Å] for the 10TAB/BNP (Fig. 3a) and O1 ··· Br2, 3.220(4) Å and O2 ··· Br1 3.161(4) Å for 14TAB/BNP (Fig. 3b). In both complexes, van der Waals contacts between carbon atoms of two naphthol groups which lay close to each other were observed (Fig. 3). The observed short contacts of the nonbonded C ··· C atoms are C29 ··· C42, 3.470(7) Å for 10TAB/BNP (Fig. 3a) and C37 ··· C50, 3.392(8) Å for 14TAB/BNP (Fig. 3b).

CONCLUSION

The packing structure of the 2:1 nTAB/BNP (where n = 10, 14) crystal complexes is unique and different from the 1:1 complexes of both short and long alkyl chain substituted monoalkyltrimethylammonium halides with BNP as well as those of 1:1 and 2:1 complexes of

monoalkyltrimethylammonium salts with planar aromatic molecules [1–6]. The host–guest ratio plays a significant role in the packing mode observed in the crystal complexes of monoalkyltrimethylammonium bromides with BNP. The manner in which the 14TAB molecules lay parallel to the naphthol moieties are similar to that observed in 2:1 complex of 10TAB/BNP. As observed in 2:1 complex of 10TAB/BNP [9], the crystal structure of 14TAB/BNP also revealed that one of the alkyl chains has an *all trans* conformation, whereas the second alkyl chain does not have *all trans* conformation but has at least a *gauche* conformation. Increasing the length of the lipid chain does not inhibit the formation of crystal complex between the monoalkyltrimethylammonium bromide with BNP. In both crystal complexes (10TAB/BNP [9] and 14TAB/BNP), the complexes are stabilized by mainly the intermolecular hydrogen bonding between the bromide anions and OH groups of BNP.

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