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THE CRYSTAL STRUCTURE OF 1:2 MOLECULAR COMPLEX OF OCTYLTRIMETHYLAMMONIUM BROMIDE WITH R-(+)-1,1′-BI-2-NAPHTHOL

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The complex formed between octyltrimethylammonium bromide (8TAB) and (R)-(+)-1,1′-bi-2-naphthol (RBNP) crystallizes in the monoclinic space group $P2_1$ with one crystallographically independent 8TAB molecule and two crystallographically independent RBNP molecules in the asymmetric unit. The crystal structure demonstrates that the nonplanar shape of the RBNP molecule affects the packing mode of the alkyl chains. The host:guest ratio as well as the length of the alkyl chain play significant roles in the packing structure of the complex. The alkyl chain does not have an all-trans fully extended conformation but one which is bent. The hydrogen bonds and C-H…π interactions stabilize the crystal structure of the complex.

Keywords: monoalkylammonium bromides; R-(+)-1,1′-bi-2-naphthol; molecular recognition; host:guest; supramolecular chemistry; molecular complex

INTRODUCTION

In host-guest complexation studies, the concept of molecular recognition has been found to be important for a better understanding of the complexation phenomenon. The molecular recognition between complexing partners is directed by specific intermolecular forces (e.g., hydrogen

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bonding) as well as by steric complementarity. The complexes formed between onium salts (e.g., monoalkyltrimethylammonium halides) and aromatic molecules do so through molecular recognition phenomenon. Recently, Toda et al. [1] reported that, 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. The complex crystallizes in the orthorhombic space group $P2_12_12_1$.

However, the selective recognition of (+) or (−)-BNP by a nonchiral amphiphilic molecule is a challenging and difficult task yet to be achieved. As an initial approach, we have chosen to investigate the crystal complexes of monoalkyltrimethylammonium halides with RBNP or BNP in order to understand the molecular recognition phenomenon which exists between a nonchiral onium salt and a chiral or racemic aromatic molecule. This knowledge will be useful for future applications, such as separation processes.

In our recent article [2], we reported that a nonchiral onium salt (hexyltrimethylammonium bromide, hereafter 6TAB) interacts with RBNP to form a 1:1 complex (6TAB/RBNP). The complex crystallizes in the monoclinic space group $P2_1$. The molecules of the 6TAB/RBNP complex are held in their aggregates by hydrogen bonds and C-H$\ldots\pi$ interactions. The crystal structure revealed that the packing arrangement of the 6TAB molecules with the RBNP (nonplanar aromatic molecule) molecules is different from those observed in complexes of monoalkyltrimethylammonium bromides with planar aromatic molecules [3–7]. It was observed that the length of the alkyl chain and nonplanar shape of the RBNP molecule play significant roles in the packing structure observed in the 6TAB/RBNP complex. Thus, we were motivated to increase the length of the alkyl chain and probe its effect on the packing structure as well as the host:guest ratio in the series of crystal complexes of both short and long alkyl chain-substituted monoalkyltrimethylammonium halides with RBNP. After several attempts to obtain such crystal complexes, we succeeded in obtaining the crystal complex of octyltrimethylammonium bromide (hereafter, 8TAB) with RBNP. Thus, in this manuscript we report on the molecular complex of 8TAB/RBNP.

EXPERIMENTAL METHODS AND CRYSTAL STRUCTURE DETERMINATION

Preparation of 8TAB Adduct of RBNP

The sample of RBNP and 8TAB were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). The 8TAB adduct of RBNP (8TAB/RBNP)

was prepared by treating 8TAB with RBNP in the molar ratio of 1:1 in an ethylacetate/acetone (2 ml/8 ml) solvent mixture. The mixture was simultaneously stirred and warmed at 303–313 K for 20 min in a 10 ml glass bottle. The resulting warmed mixture was then covered with perforated plastic thin wrap and kept in an incubator at 293 K for 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 8TAB/RBNP complex were 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 25 carefully centered reflections in the range of $79 < 2\theta < 80°$. The intensity data were collected at 298 K in the ω-2θ scan mode with a scanning speed of 8°/min and scanning widths of $\Delta w = (1.52 + 0.30 \tan\theta)°$, respectively. Three reference reflections were measured after every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was also applied in the data. The data were corrected for Lorentz and polarization effects. The crystal data are shown in (Table 1).

TABLE 1 Crystal Data of 1:2 Complex of 8TAB/RBNP

Complex	8TAB/RBNP
Molecular formula	$C_{51}H_{50}O_4NBr$
Formula weight	846.91
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	8.536(2)
b/Å	29.219(2)
c/Å	9.073(2)
β/°	105.40(2)
Volume/Å^3	2181.7(7)
Z	2
D_{calc}/gcm^{-3}	1.249
F(000)	860
Crystal dimensions/mm	$0.20 \times 0.20 \times 0.20$
Maximum 2θ	130
T/K	298

Determination and Refinement of the Crystal Structure

The crystal structure of the complex was solved by direct methods (SIR92) [8] and expanded using Fourier techniques (DIRDIF94) [9]. The non-hydrogen atoms of the complex were refined anisotropically. We could not find the position of the hydrogen atoms attached to O(1) and O(2) of both RBNP adducts in the difference Fourier map, thus they were not included in the calculation. All of the other hydrogen atoms were introduced by geometrical calculations but not refined.

The C-C bonds in 8TAB were restrained to 1.520 Å with a weight of 0.0005 and all the N-C bonds were restrained to 1.490 Å with a weight of 0.0005. The atomic distances between C1 ··· C2, C1 ··· C3, C1 ··· C4, C2 ··· C3, C2 ··· C4, C3 ··· C4, C4 ··· C6, C6 ··· C8, C8 ··· C10, C7 ··· C9, and C9 ··· C11 were restrained to 2.520 Å. The final cycles of full matrix least-squares refinement were based on 2609 reflections, 513 variable parameters, and 21 geometrical restraints. The function minimized was $\sum w(|\,F_o\,| - |\,F_c\,|)^2$, where $w = 1/\sigma^2(F_o)$. The final R-values were $R = 0.080$ and $R_w = 0.0105$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and $-0.84 e^-/Å^3$. 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 [10]. Neutral atom scattering factors were taken from Cromer and Waber [11]. The final atomic coordinates and anisotropic thermal parameters, torsion angles, bond lengths, and bond angles for the complex are deposited at the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CBZ, 1EZ, UK. The deposition reference number is 160234.

RESULT AND DISCUSSION

Molecular Structure of 8TAB/RBNP Complex

The molecular structure and atomic numbering scheme of the title complex are shown in (Fig. 1). The asymmetric unit of the complex consists of one crystallographically independent molecule of 8TAB (host) and two crystallographicaly independent molecules of RBNP (guest). In the host molecule, the ammonium cation and bromide anion (Br^-) constitute the hydrophilic region, while the alkyl chain constitutes the hydrophobic region. The hydrophilic head group is rigid, while the hydrophobic tail part is not. The charged N atom has a tetrahedral structure with four carbon atoms. The naphthol groups in the RBNP molecule have a rigid aromatic ring conformation. The RBNP molecule is nonplanar due to the effect of steric influences of the two adjacent neighboring oxygen atoms on each of the naphthol moieties.

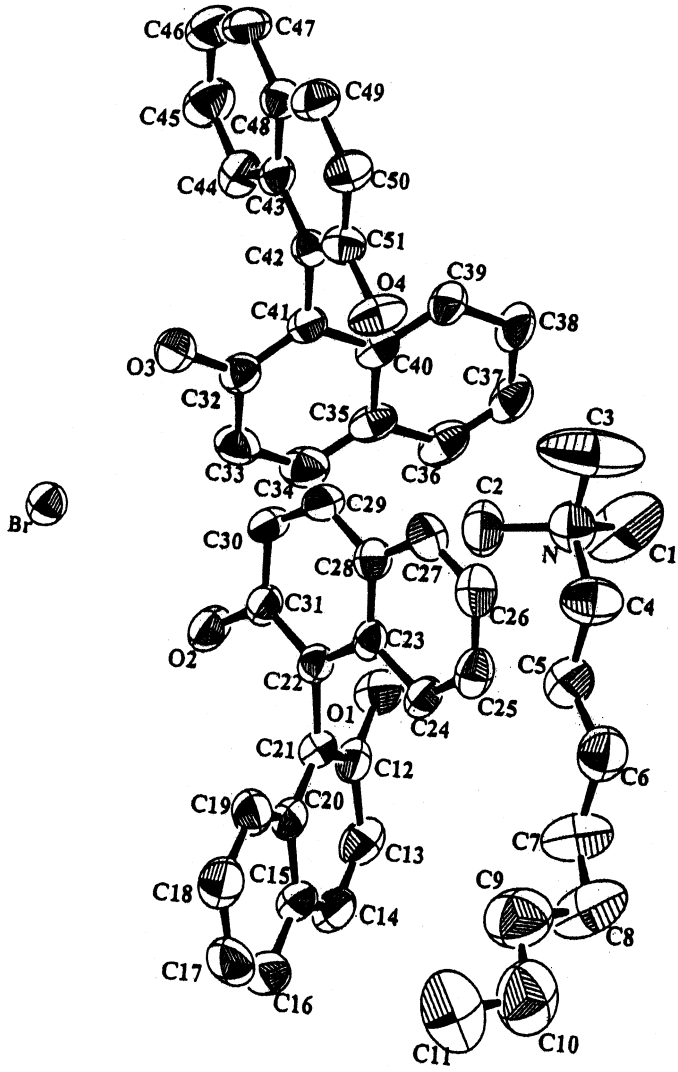

FIGURE 1 The molecular structure and atomic numbering of 8TAB/RBNP. The 40% probability ellipsoids are shown. Hydrogen atoms are omitted for clarity.

The bond distances and angles in the 8TAB molecule are normal and within the range of values as observed in other monoalkyltrimethylammonium halides [12] and in their complexes [3–7]. The 8TAB molecule has a normal geometry with an average C-C bond length and C-C-C bond angle values of 1.52(3) Å and 111.7(3)°, respectively, while the

average N-C bond length and C-N-C bond angle are 1.531(5) Å and 109.5(7)°, respectively. The bond lengths and angles are in the range of 1.52(1) to 1.520(10) Å for C-C, and from 110.5(6) to 112.0(1)° for C-C-C, and from 1.53(1) to 1.533(10) Å for N-C, and from 109.4(6) to 109.7(6)° for C-N-C. With the exception of the *gauche* conformation at C7-C8 (84(2)°), the torsion angles in the alkyl chain are within the range of 180 ± 15°. The alkyl chain does not have an *all-trans* fully extended conformation but is bent. The mean deviation from plane in naphthol planes (1) and (2); (3) and (4) are 0.0188 and 0.0193Å; 0.0092 and 0.0094Å, respectively. The dihedral angle between the two naphthol planes in each case is defined by: O1, C12, . . . ,C12 and O2, C31, . . . ,C22 is 74(7)°; O3, C32, . . . ,C41 and O4, C51, . . . ,C42 is 81(8)°. The RBNP molecules adopt the *cisoid* [13] conformation in each case. The C-C bonds joining the two naphthol rings in each of the RBNP molecules are not significantly different from each other. In both cases, the C-C bond length is 1.500(7) Å. The average values of the C-C bond lengths and C-C-C bond angles in the naphthalene ring of the naphthalene groups (1) and (2); (3) and (4) are: 1.392(4) Å, 120.4(6)°, and 1.402(7) Å, 119.9(6)°; 1.397(6) Å, 120.4(6)°, and 1.400(5) Å, 120.3(6)° respectively. These values suggest that the naphthalene rings do not differ significantly from each other, and no deformation is observed in the rings. The thermal ellipsoids shown in (Fig. 1) suggest reasonable and normal temperature factors of the atoms in both 8TAB and RBNP molecules.

Packing Structure and Intermolecular Interactions in the Complex

The crystal packing arrangement of the complex viewed along the *a*-axis is illustrated in (Fig. 2). The complex crystallizes in monoclinic space group $P2_1$. The unit cell (Fig. 2) consists of two 8TAB molecules and four RBNP molecules, since the Z-value (Table 1) is 2 and the host:guest ratio is 1:2. In the unit cell, the 8TAB molecules are not arranged in an interdigited fashion as observed in complexes of monoalkyltrimethylammonium halides with planar aromatic molecules [3–7]. The packing arrangement in the 1:2 complex of 8TAB/RBNP is completely different from that observed in the 1:1 complex of 6TAB/RBNP [2], and those of monoalkyltrimethylammonium halides with planar aromatic molecules [3–7]. The alkyl chains adopt a bent conformation and may be attributed to the effect of the nonplanar shape of the RBNP molecule, i.e., placing a naphthol plane almost normal to the alkyl chain axis. These observations in the crystal structure suggest that the nonplanar shape of the RBNP molecule, the host:guest ratio, and length of the alkyl chain all play significant roles in the packing structure of the complex.

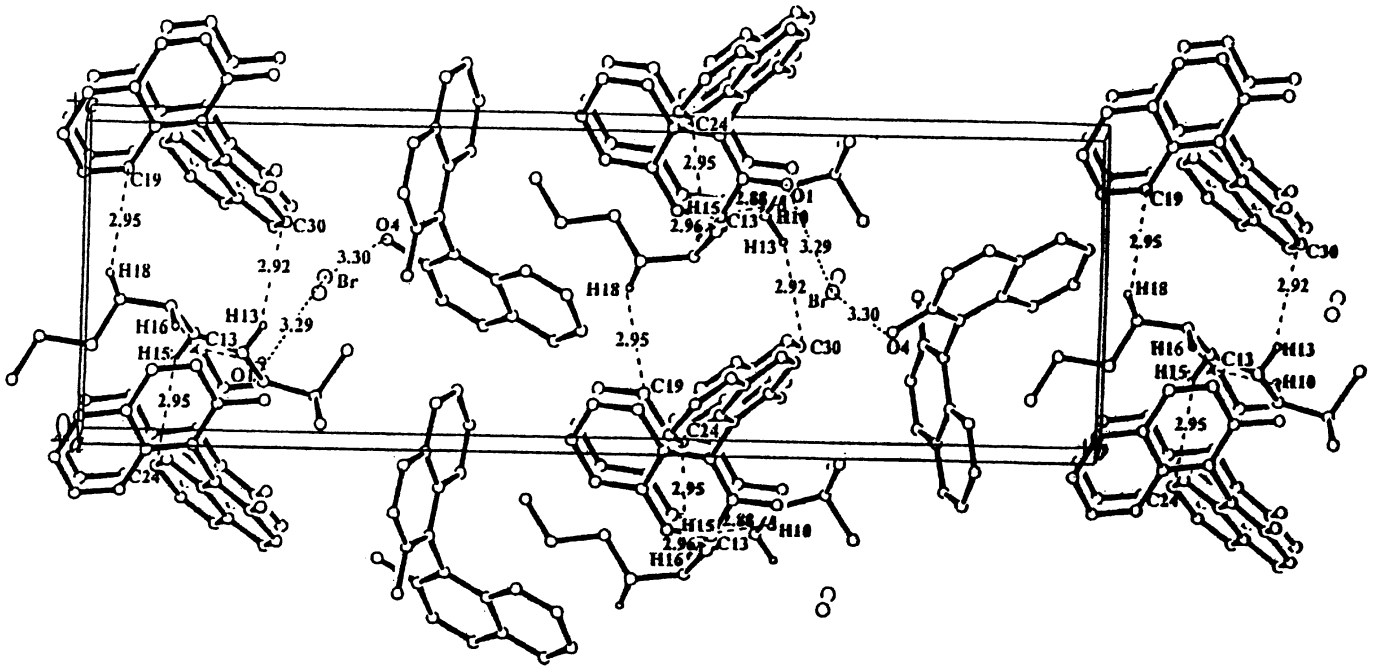

FIGURE 2 The hydrogen bonds and C-H . . . π interactions observed in the crystal structure of 8TAB/RBNP. The broken lines represent C-H . . . π interactions, while the dotted lines represent hydrogen bonds.

Since the H-atoms of the hydroxyl group of RBNP molecules were not located in the difference Fourier map, the criterion for hydrogen bonding was based on the short contact distances between non-H atoms with values less than the sum of their van der Waals radii. In the crystal structure (Fig. 2), only one of the OH groups in each of the RBNP molecules participated in the hydrogen bonding scheme with the bromide anion. The hydrogen bonds that contribute to the stability of the crystal structure are; Br . . . O1,3.290(5) Å and Br . . . O4, 3.300(6) Å (Fig. 2). The C-H . . . C distances between hydrogen atoms of the alkyl chain 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 (2.97 Å) [14] are shown in (Fig. 2).

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