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Molecular and Crystal Structures of Dodecyltrimethylammonium Bromide and its Complex with *p*-Phenylphenol

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The crystal structures of dodecyltrimethylammonium bromide (Space group of $P2_1$, $a = 5.638(2)$, $b = 7.244(1)$, $c = 21.554(2)$Å, $\beta = 93.06(2)^\circ$, $R = 0.083$ for 1425 reflections) and its complex with *p*-phenylphenol (Space group of $P2_1/m$, $a = 11.191(2)$, $b = 7.462(1)$, $c = 27.413(1)$Å, $\beta = 96.738(7)^\circ$, $R = 0.076$ for 3679 reflections) were determined by the X-ray diffraction method. Both crystals have the smectic layer structure stacked along the *c*-axis and the molecular plane layer structures stacked along the *b*-axis. In the crystal of the complex, the guest molecules (*p*-phenylphenol) are included between the host (dodecyltrimethylammonium bromide) molecules to form many interactions with them. The arrangement of the host molecules along the *c*-axis is affected by the guest molecules, but the arrangement of them along the *a*- and *b*-axis are almost conserved through the inclusion of guest molecules.

Keywords: X-ray crystal analysis; amphiphilic molecules; surfactants; complex formation; dodecyltrimethylammonium bromide

INTRODUCTION

Amphiphilic molecules, such as fatty acids, surfactants and lipids are well known to form the smectic layer structure in their solid states. These crystal

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*Corresponding author. Abbreviations: DTAB, dodecyltrimethylammonium bromide; DTA, dodecyltrimethylammonium; pPP, *p*-phenylphenol.

structures are very useful as models of the liquid crystals and the lipid bilayer biomembranes [1].

Dodecyltrimethylammonium bromide (DTAB) is one of the most widely used cationic surfactants as a detergent in chemical industries. The molecular and crystal structures of such cationic surfactants at atomic level are very important to elucidate the mechanism of surfactant activities. Moreover, these cationic surfactants have an interesting property in that they easily form the crystalline complexes with various organic molecules as guest molecules [1,2]. The interaction between cationic surfactants (host) and organic compounds (guest) should be very strong and specific, because the complexes are obtained by just mixing them in a mortar with a pestle and because the selectivity of guest molecules is found [2]. Therefore, it is very interesting to determine the crystal structures of complexes between them and to know how these cationic surfactants interact with other molecules. Although the crystal structures of hexadecyltrimethylammonium bromide (HTAB) [3] and its complexes with various phenol derivatives have been reported [2], the molecular packing structures and the interactions between host and guest molecules have not been discussed in detail. The crystal structures of complexes of dodecyltrimethylammonium chloride (DTAC) with catechol and hydroquinone are also reported [4,5]. However the molecular packing structures of the DTAC complexes are apparently different from the present study of the DTAB complex, in spite of the same host molecule (DTA).

Here, we report the crystal structures of DTAB and its complex with *p*-phenylphenol (pPP) and the comparison between them.

EXPERIMENTAL

Crystallization and Data Collection

The DTAB was dissolved in ethylacetate-acetone (1:1) solution at 50°C and kept in the incubator at 20°C. The plate-like crystals were grown within a few days. After dissolving of (1:2) molar ratio of DTAB and pPP in ethylacetate-acetone (1:1) solution at 70°C, the slow cooling of the solution to room temperature gave the plate crystals of the DTAB/pPP complex.

A crystal of DTAB with the dimensions of 0.60 × 0.20 × 0.10 mm and a crystal of DTAB/pPP complex with the dimensions of 0.60 × 0.20 × 0.10 mm were mounted on glass fibers. Diffraction data were collected by a Rigaku AFC7R diffractometer on a Rigaku rotation anode X-ray generator with graphite monochromated CuKα radiation. Cell constants and orientation matrices for data collection were determined by a least-squares refinement using 25 carefully centered reflections in the range of $78^\circ < 2\theta < 81^\circ$. Parameters for data collection and crystal data of both crystals are listed in Table I. Both intensity data were corrected for Lorentz and polarization effects. Absorption corrections by the empirical method (psi scan) were carried out but decay corrections were, not applied.

Structure Determination and Refinement

Both structures were solved by direct methods using the program SHELX-86 [6] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced by geometrical calculations but not refined. The final cycles of full-matrix least-squares refinement were based on 1425 reflections (all of the observed reflections), 153 variable parameters and 32 geometrical restraints for DTAB, and 3679 reflections (all of the observed reflections), 276 variable parameters and 52 geometrical restraints for DTAB/pPP. Final R-factors (calculated based on Fo) and Rw-factors (calculated based on Fo^2, $w = 1/\sigma^2(\text{Fo})^2$) are 0.083 and

TABLE I Crystal data and data collection parameters

Compound		*DTAB*	*DTAB/pPP*
Formula		$C_{15}H_{34}NBr$	$C_{15}H_{34}NBr/C_{12}H_{11}O$
Molecular weight		308.34	479.55
Space group		$P2_1$	$P2_1/m$
a/Å		5.638(2)	11.191(2)
b/Å		7.255(1)	7.462(1)
c/Å		21.554(2)	27.413(1)
β/		93.06(2)	96.738(7)
V/Å^3		880.4(4)	2273.5(5)
Z		2	1.5
μ(CuKα)/cm^{-1}		30.33	25.94
Dobs		1.14	1.15
Dcalc		1.16	1.15
F(000)		664.0	1028.0
Maximum $2\theta/^\circ$		120	120
HKL range	H	0, 6	0. 12
	K	0, 8	0, 8
	L	−24, 24	−30, 30
No. of observed reflections		Total: 1430 Unique: 1425	Total: 3896 Unique: 3679
Rint		0.04	0.02

$$R\text{int} = \frac{\sum \||Fo| - \langle |Fo| \rangle|}{\sum |Fo|}.$$

0.1095 for DTAB, and 0.076 and 0.079 for DTAB/pPP, respectively. The maximum peaks on the final difference Fourier map are 0.54e$^-$/Å^3 for DTAB and 0.32e$^-$/Å^3 for DTAB/pPP. Atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol. IV. All calculations of data collection, structure determination and refinement were performed using the teXsan crystallographic software package of the Molecular Structure Corporation [7], SHELX-86 [6] and SHELX-93 [8].

Final data may be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

RESULTS AND DISCUSSION

Molecular Structure of DTAB

A molecular structure of DTAB with atomic numbering is shown in Figure 1 [9]. All bond distances and angles of the DTA molecule are in the normal range, from 1.496(6) to 1.528(6)Å for C—C and from 109.6(5) to 119.3(7)° for C—C—C (or —N), and from 1.489(5) to 1.520(5)Å for C—N and from 108.0(4) to 112.4(6)° for C—N—C. The charged N1 atom has a tetrahedral structure with four carbon atoms, the C1, C13, C14 and C15 atoms, and forms the electrostatic interaction with Br$^-$ anions. Although, the alkyl chain has an extended structure of all-*trans* conformation, the torsion angles of C—C in the alkyl chain are in the relatively wide range, as shown in Figure 1. The torsion angles which deviated more than 10° from 180° are 165° for C1—C2, −151° for C5—C6, −160° for C6—C7 and 167° for C10—C11. This structural irregularity of the alkyl chain is also shown by the calculation of the atomic plane of the alkyl chain. The average deviation of

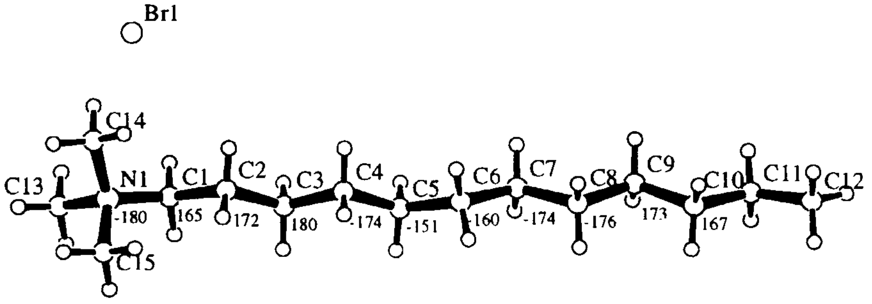

FIGURE 1 Molecular structure of a DTAB molecule with the atomic numbering and the torsion angles of the alkyl chain.

each atom from the least-squares plane calculated by the fourteen atoms from the C1 to C13 and the N1 are 0.14Å, and the largest one is 0.29Å for the C9.

Molecular Packing of DTAB Molecules

Molecular packing of DTAB molecules is shown in Figure 2 (a) (viewing from the *a*-axis), (b) (viewing from the *b*-axis) and (c) (stereo drawing). Since the space group of $P2_1$ requires the fixing of the *y*-coordinate of one atom during

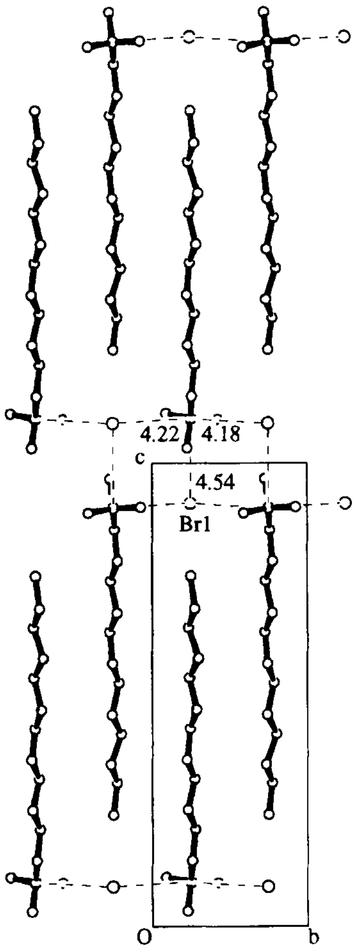

FIGURE 2a Molecular packing of DTAB molecules viewing from the *a*-axis. Possible electrostatic interactions between ammonium groups and Br^- anions are shown by dashed lines.

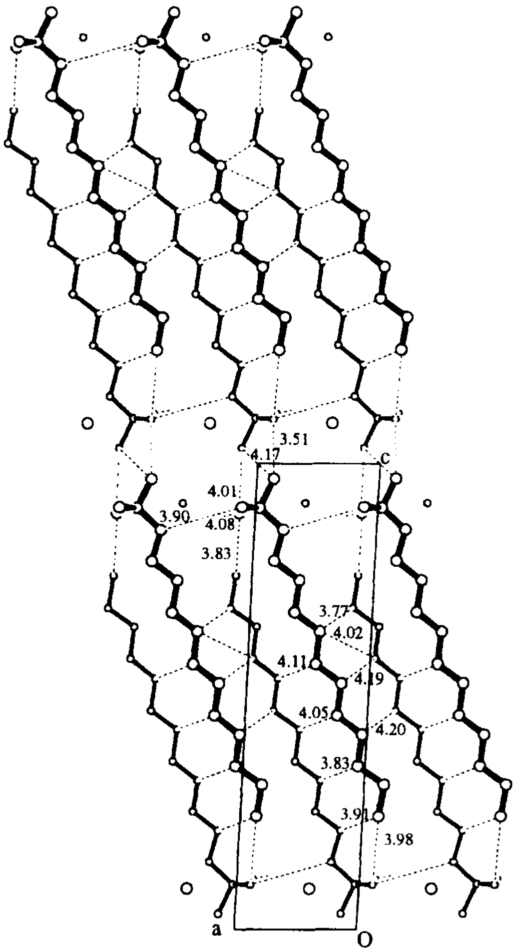

FIGURE 2b Viewing from the *b*-axis. Possible van der Waals contacts (less then 4.2Å) are shown by dotted lines. Molecules drawn by thin bonds are on the *ac*-layer at $y = 0.25$, and molecules drawn by thick bonds are on the *ac*-layer at $y = 0.75$.

the structure refinement, the N1 atom is fixed at $y = 0.25$ for the comparison with the crystal structure of DTAB/pPP complex, described later.

The DTAB molecules form the smectic layer structure stacked along the *c*-axis. Along the *b*-axis, there is also the molecular plane layer structure, where DTAB molecules are almost on the *ac*-plane of $y = 0.25$ and $y = 0.75$. For a clear discussion, the layer stacked along the *c*-axis is called the smectic-layer and the layer stacked along the *b*-axis is called the *ac*-layer. The *ac*-layer consists DTA molecules oriented in the same direc-

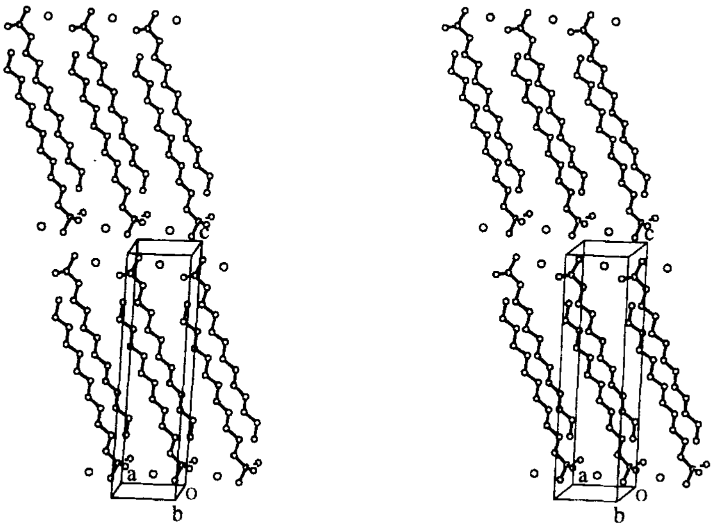

FIGURE 2c Stereo Drawing of molecular packing of DTAB molecules.

tion. The angle between the longest principal axis of DTA molecule and the *a*-axis is 68°.

Along the *c*-axis, the hydrophilic and hydrophobic regions are alternately found. The hydrophilic region is formed by the ammonium groups and Br^- anions. The distances between the N1 atom and the Br1 anion in the same *ac*-layer is 4.54Å, and in the adjacent *ac*-layers are 4.18Å and 4.22Å, as indicated in Figure 2(a). The methyl groups attached to the ammonium group make van der Waals contacts with the neighbor molecule in the same *ac*-layer; the distances of the C14—C1* (*means the atom of the symmetry-operated molecule) and C15—C1* are 4.08 and 3.90Å, respectively. They also make van der Waals contacts with the methyl groups of the molecules operated by the 2_1 axis in the adjacent *ac*-layer; the distances of the C13—C13*, C13—C14*, C15—C13* and C15—C1* and 4.17, 3.51, 4.01 and 3.83Å, respectively. The hydrophobic region is formed by the alkyl chains and there are many van der Waals contacts between the alkyl chains of DTA molecules in the adjacent *ac*-layer, as shown in Figure 2(b).

Molecular Structures of DTAB and pPP in the DTAB/pPP Complex

In the crystal of DTAB/pPP complex, two DTAB molecules and a pPP molecule exist in an asymmetric unit. However, both of DTAB and pPP molecules are located on the crystallographic mirror plane, so two halves of DTAB molecules, named Mol A and Mol B, and a half of a pPP molecule are independent. The structure of them with atomic numbering is shown in Figure 3. The DTA molecules are located on the a mirror plane at $y = 0.25$, and the pPP molecule and Br^- anions are located on the another mirror plane at $y = 0.75$ in Figure 3.

All bond distances and angles of the DTA molecules are in the normal range from 1.502(5) to 1.536(5)Å for C—C and from 106.3(4) to 117.0(4)° for C—C—C (or —N), and from 1.497(5) to 1.521(4)Å for C—N and from 106.2(4) to 112.2(2)° for C—N—C. All bond distances and angles of the pPP molecule, except the bond distance of 1.458(9)Å for the C4P—C7P, also are in the normal range from 1.362(9) to 1.390(6)Å for C—C and from 116.7(7) to 127.3(8)° for C=C—C (or —O), and 1.362(9)Å for C—O.

The charged N1 atoms of both Mol A and Mol B have tetrahedral structures with four C atoms, the C1, C13, C14 and C14* atoms, and form the electrostatic interaction with Br^- anion; the distances between them are 4.32Å for Mol A, and 4.28Å for Mol B in Figure 3. The alkyl chain of both Mol A and Mol B have an extended structure of all-*trans* conformation with C—C torsion angles of 180°, because both molecules are on the crystallographic mirror plane.

The pPP molecule adopts the plane structure with the bond distance of 1.458(9)Å between the C4P and C7P atoms, indicating the conjugate system of a coplanar biphenyl ring. In the crystal structures of pPP itself [10], both of the plane structures and the twisted structures were found, which sug-

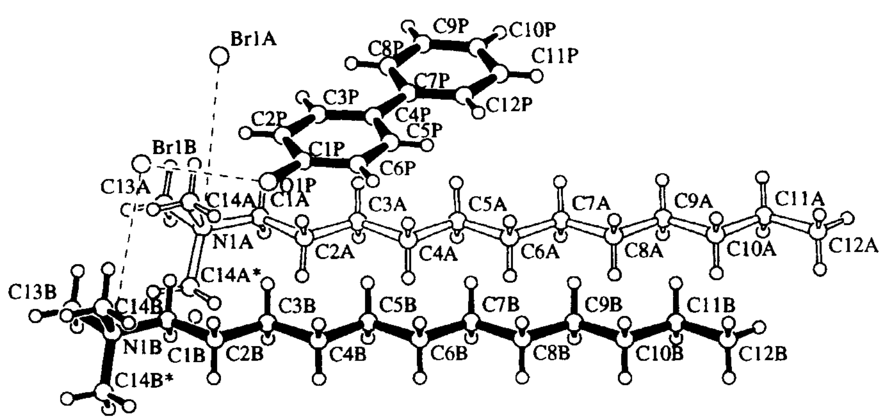

FIGURE 3 Molecular structures of a DTAB/pPP complex with the atomic numbering. Mol A is drawn by open bonds, and Mol B and a pPP molecule by solid bonds. Possible electrostatic interactions are shown by dashed lines.

gests that the structural energies between the plane and twisted structures are almost equal. The angles between two phenyl rings of the twisted structures are about 23°, to avoid the steric hindrance between hydrogen atoms attached to phenyl rings. The pPP molecules in the DTAB/pPP complex selects the plane structure by interactions with the alkyl chains of DTAB molecules, especially Mol A, mentioned later.

The distance between the O1 atom of pPP and Br1B anion is 3.26Å, meaning the formation of a hydrogen bond, though the hydrogen atom attached to the O1P atom could not be located in the final difference Fourier map. In addition to this hydrogen bond, the Br1A anion seems to form the weak hydrogen bonds of Br1A—H—C3P and Br1A—H—C8P, because hydrogen atoms attached to the C3P and C8P atoms are pointing to the Br1A anion. However, in practice, these distances are 3.78Å from the C3P atom, and 4.21Å from the C8P atoms, so there are no attractive interactions, such as the partial hydrogen bonds, except van der Waals interactions between them.

Molecular Packing of DTAB/ pPP Complexes

Molecular packing of DTAB/pPP molecules is shown in Figure 4 (a) (viewing from the *a*-axis), (b) (viewing from the *b*-axis) and (c) (stereo drawing). All of the non-hydrogen atoms except the C14 and C14* atoms are in the plane of $y = 0.25$ or $y = 0.75$. The DTAB and pPP molecules form the smectic layer structure along the *c*-axis and the *ac*-layer structure along the *b*-axis, as found in the crystal structure of DTAB itself.

Surprisingly, in spite of the inclusion of pPP molecules, the crystal structures of the DTAB itself and the DTAB/pPP complex are very similar to each other. Both of their *ac*-layer structures are almost the same, including the inclination of the DTA molecules; the angles between the *a*-axis and the Mol A and/or Mol B are about 65°. The length of the *a*-axis of the DTAB/pPP complex is almost twice the value (11.19Å) compared to that of the DTAB itself (5.64Å). It is because Mol A and Mol B are approximately related by the translation of 0.5 along the *a*-axis, which corresponds to the translation of 1.0 in the crystal of DTAB itself. The only major difference between them is the insertion of the pPP molecule between the terminal C12 atom of the alkyl chain, and the Br^- anion in the same *ac*-layer, so that the length of the *c*-axis should be elongated from 21.55Å (in the DTAB crystal itself) to 27.41Å.

Along the *c*-axis, hydrophilic and hydrophobic regions are alternately found, as in the crystal of DTAB itself. The hydrophilic region is formed by

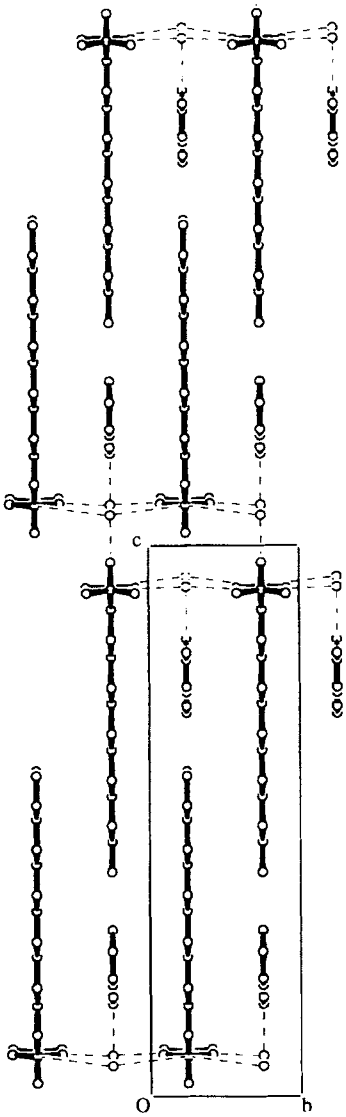

FIGURE 4a Molecular packing of DTAB/pPP complexes viewing from the *a*-axis. Possible electrostatic interactions between ammonium groups and Br⁻ anions are shown by dashed lines.

the ammonium groups, Br⁻ anions and the O1P atom of the pPP molecule, and the distances between them are 4.32Å for the Br1A—N1A, 4.28Å for the Br1A—N1A*, 4.28Å for the Br1B—N1B, 4.80Å for the Br1B—N1B*, and 3.26Å for the Br1B—O1P. Interactions of methyl and methylene groups

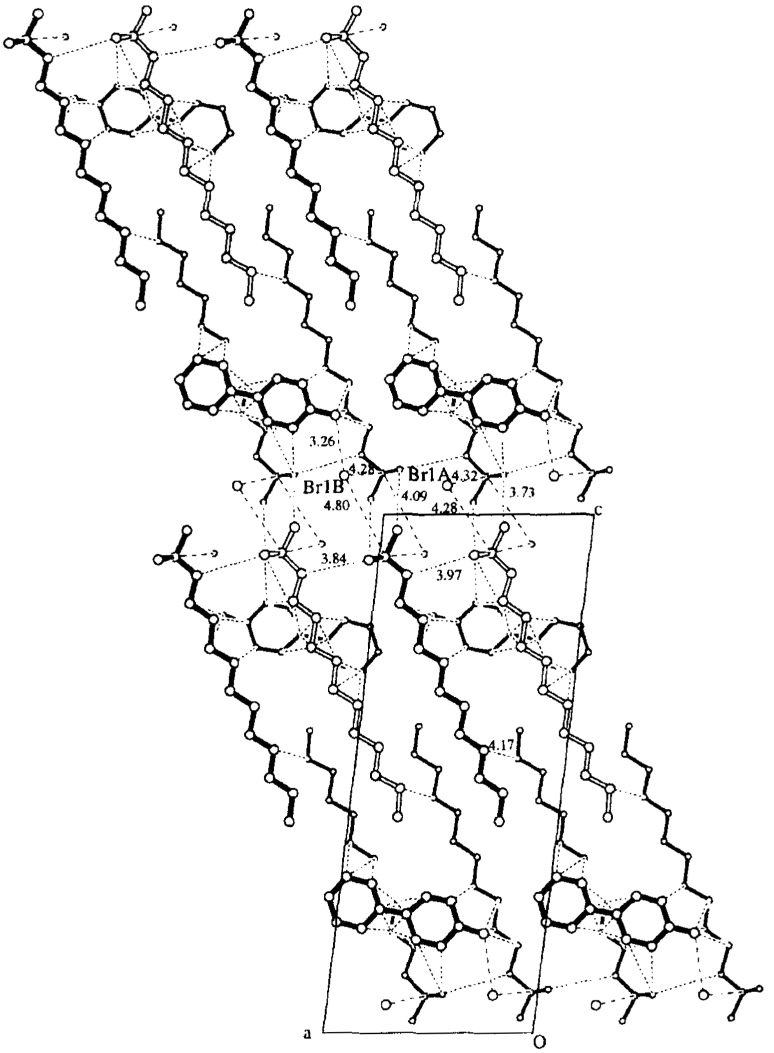

FIGURE 4b Viewing from the *b*-axis. Mol As are drawn by open bonds, and Mol Bs and pPP molecules by solid bonds. Possible electrostatic interactions between ammonium groups and Br^- anions, and possible van der Waals contacts (less than 4.2Å) are shown by dashed lines and dotted lines, respectively. Molecules drawn by thin bonds are on the *ac*-layer at $y = 0.25$, and molecules drawn by thick bounds are on the *ac*-layer at $y = 0.75$.

are also almost equivalent to those of the crystal of DTAB itself, and these distances are 3.97Å for the C14A—C1B, 3.84Å for the C14B—C1A, 3.73Å for the C13A—C14A*, and 4.09Å for the C13B—C14B*. Because these electrostatic interactions between ammonium groups and Br^- anions and

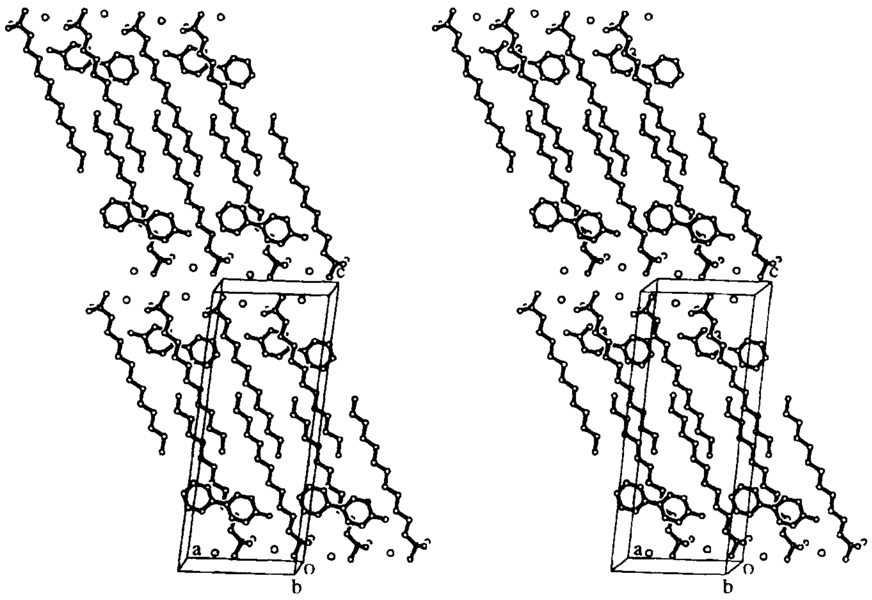

FIGURE 4c Stereo Drawing of molecular packing of DTAB/pPP complexes.

van der Waals contacts of methyl and methylene groups are almost conserved through the inclusion of pPP molecules, they are thought to be very strong and to contribute to the stable molecular packing of the host (DTA) molecules extensively. The hydrophobic region is formed by the alkyl chains of the DTA molecules and the pPP molecules. There are not so many van der Waals contacts between the alkyl chains of DTA molecules as in the crystal structure of DTAB itself, however, the alkyl chains form van der Waals contacts with the phenyl rings of the pPP molecule. Especially, the alkyl chain of Mol A interacts with the center of the pPP molecule. The pPP molecule is sandwiched by the alkyl chains of DTA molecules with the plane structure, as shown in Figure 4(a). The pPP molecules need to have a plane structure, to occupy the space between the planar DTA molecules and to form favorable van der Waals contacts with them.

MolA and MolB are related by non-crystallographic translation symmetry, as described above. This translation symmetry is broken by not only the pPP molecules but also Br^- anions. Because the hydrogen bond between the Br1B anion and the O1P atom partially compensates the charge of the Br1B anions, the distance of 4.80Å between the Br1B anions and the N1B* atoms in the same *ac*-layer is longer than the distance of 4.28Å in

Mol A (Br1A—N1A*). Consequently, the Br anions are located in a zigzag arrangement along the *a*-axis to break the relationship of translation symmetry between Mol A and Mol B.

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