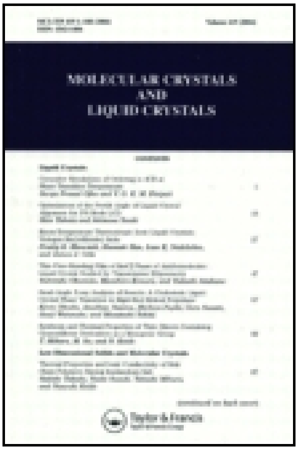

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The Crystal Structure of Decyltrimethylammonium Chloride with Rac-1,1′-Bi-2-Naphthol

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The Crystal Structure of Decyltrimethylammonium Chloride with Rac-1,1′-Bi-2-Naphthol

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The X-ray structure analysis of 1:1 crystal complex of decyltrimethylammonium chloride with rac-1,1′-bi-2-naphthol (hereafter, 10TAC/BNP) yielded a triclinic lattice with $P\bar{1}$ *symmetry,* formula $C_{33}H_{42}NClO_3$, formula weight *536.15,* crystal size $0.10 \times 0.20 \times 0.10\,mm^3$, $a = 9.999(1)$ Å, $b = 19.420(1)$ Å, $c = 8.977(9)$ Å, $\alpha = 92.845(8)^\circ$, $\beta = 112.718(7)^\circ$, $\gamma = 98.396(7)^\circ$, $V = 1579.9(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.135\,g\,cm^{-3}$, $2\theta max = 120.2^\circ$, $m.p = 168.7^\circ C$, *and the asymmetric unit consists of a molecule each of 10TAC, BNP, and water. The crystal structure shows a distinct similarity in the packing structure observed in crystal complexes of monoalkyltrimethylammonium halides with planar aromatic molecules. The arrangement of the naphthol planes as per controlled by the hydrogen bond network plays significant role in the packing structure. The combined actions of hydrogen bonding, electrostatic interactions and C-H*$\cdots\pi$ *interactions contribute to the stability and formation of the crystal complex.*

Keywords: complexes; decyltrimethylammonium chloride; diffraction; Hydrogen bonding; interactions; racemic

1. INTRODUCTION

The use of hydrogen bond interactions to control molecular arrangements and establish well-defined supramolecular architectures is a major current topic. Crystal structure determinations primarily serve a better understanding of the rules which govern molecular associations and packing [1]. The understanding of crystal packing and

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intermolecular interactions in host-guest chemistry through crystal structure studies of supramolecules (complexes) has enhanced developments made by material scientists, supramolecular chemists, and biotechnologists [2]. The inclusion of the guest molecule by the host molecule to form a complex involves molecular recognition phenomena. The molecular recognition between the host and guest molecules is directed by specific intermolecular forces (e.g., hydrogen bonding) as well as steric complementarity.

Strong directing intermolecular hydrogen-bonding interactions have been important in the construction of supramolecules. Understanding the intermolecular interactions between non-chiral surfactant molecules with non-planar aromatic molecules with functional groups is essential for the proper design of molecular networks that can enhance the knowledge and technology on approaches to suitable separation science techniques.

Crystal structure studies on many complexes of monoalkyltrimethylammonium halides with rac-1,1′-bi-2-naphthol (hereafter, BNP) have been reported by our group, and the crystal structure of a complex yet to be reported is that of decyltrimethylammonium chloride (hereafter, 10TAC) with BNP. Thus, we report for the first time on this crystal structure for the purpose of contributing knowledge on packing structure of 10TAC/BNP complex.

In view of the importance of packing patterns of guest molecules between host molecules in molecular crystals, we have analyzed the arrangement of packing motifs of aromatic naphthol planes of BNP between the zig-zag and interdigidated alkyl chains arrangement of 10TAC, under the influence and control of hydrogen bonding network on the arrangement of the naphthol planes as well as packing structure of the alkyl chains in the 10TAC/BNP complex. The formation of the 10TAC/BNP complex in the mixed powdered state was also investigated by means of powder diffraction pattern studies.

2. EXPERIMENTAL

2.1. X-Ray Powder Diffraction Studies

In order to obtain X-ray powder diffraction patterns of the molecular complex, the complex was prepared by grinding both 10TAC (host) and BNP (guest) compounds (molar ratio 1:1) together in an agate mortar using pestle for 45 minutes. The ground powdered mixture of host and guest components was kept unto the surface of the glass sample holder and placed in the sample pot set up in the powder diffraction diffractometer. The X-ray diffraction of powdered samples of host/guest mixture of the complex was recordered using a Rigaku RAD-C diffractometer with Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 30 mA and with a scan speed of 10°/min. The X-ray powder diffraction patterns for the complex was compared with the stimulated powder patterns based on atomic coordinates of the structure analyzed.

2.2. Preparation of Crystal Complex and Structure Determination

The 10TAC/BNP crystals were crystallized from 8 mL acetone solution within 24–36 hrs by slow evaporation method in an incubator at about 293 K. A four-circle diffractometer (Rigaku AFC5 R) fitted with graphite monochromatized CuKα radiation ($\lambda = 1.5418$ Å) was used for data collection. 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 $46.63 < 2\theta < 65.76°$. The intensity data were collected at 298 K in the ω-2θ scan mode with scanning speed of 8° and scanning widths of $\Delta w = (1.31 + 0.30\tan\theta)°$. Three reference reflections were measured after every 100 reflections. Small intensity decreases (0.2%) were observed, thus decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied together with Lorentz and polarization corrections. The crystal structure was solved by direct methods (SIR92) [3] and expanded using Fourier techniques (DIRDIF) [4]. The refinement of the crystal structure was made by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to O1, O2, and Ow of water could not find its position in the difference Fourier map, but were included at calculated positions, with O-H = 0.86 Å. All other H atoms were placed in idealized positions with C-H distances of 0.99 Å for the secondary (CH_2) group and 1.00 Å for the tertiary (CH) group. The H atoms were treated using a riding model. The final cycles of full-matrix least-squares refinement were based on 1787 observed reflections, 343 variable parameters, and 28 geometrical restraints. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w = 1/\sigma^2(Fo)$. The maximum and minimum peaks on the final difference Fourier map was 0.38 and $-0.29e^-/Å^3$. The goodness of fit, final crystallographic R-(calculated based on F), and R_w-factor (calculated based on F^2) were 1.99, 0.095, 0.124, respectively. Atomic scattering factors were taken from Cromer and Waber [5]. All calculations on data collection, structure determination, and refinement were performed using the teXsan crystallographic software package of the Molecular Structure Corporation [6]. The experimental parameters, atomic coordinates, bond lengths, bond angles, torsional angles and thermal parameters can be obtained upon request from the *Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.*

3. RESULTS AND DISCUSSION

3.1. Powder Diffraction Patterns of the Complex

It was found that the X-ray diffraction pattern of the mixed powder of the samples is essentially similar to the pattern calculated from three-dimensional intensity data of the complex. The strong peaks in the powder diffraction patterns (Fig. 1) correspond to the peaks in the simulated diffraction patterns, which suggests that 1:1 (molar ratio) complex crystals can be obtained by crystallization from solution and also by the method of mixing powdered samples in a mortar.

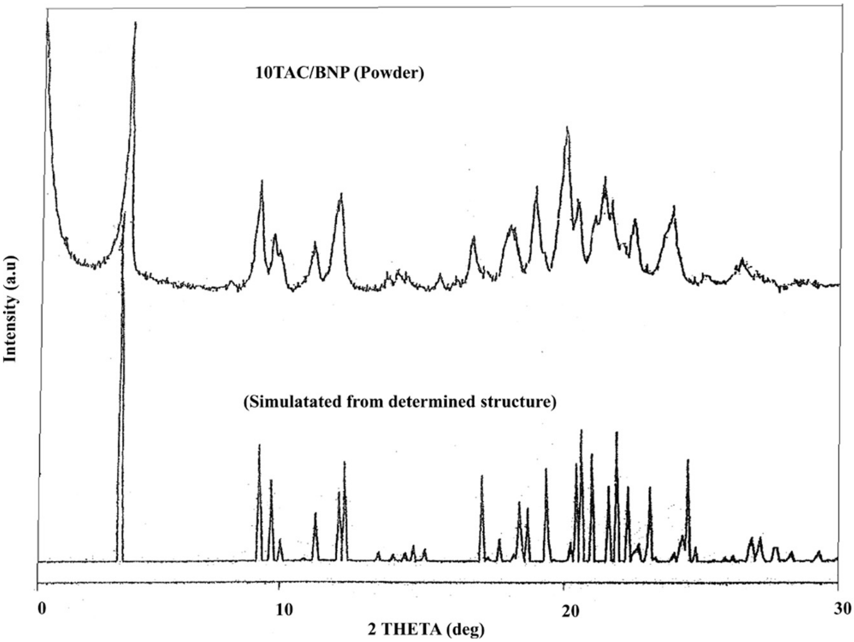

FIGURE 1 The X-ray powder diffraction patterns of mixed powdered sample and simulated powder patterns of 10TAC/BNP.

3.2. Description of Crystal Structure

The molecular structure of 10TAC/BNP with atomic numbering (Fig. 2) shows an asymmetric unit that consists of a molecule each of 10TAC, BNP, and water, as well as the thermal ellipsoid of the molecular structure showing the temperature factor of C6 to C13 generally large, and could be attributed to the effect of the role played by the flexible host molecules as space filler of the cage built by the rigid BNP molecules. The BNP molecule is non-planar due to the effect of steric influences of the adjacent neighboring oxygen atoms on each of the naphthol moieties, whilst in the 10TAC molecule the alkyl chains exhibits a ziz-zag conformation. The head part (ammonium cation) of 10TAC is the hydrophilic region of the molecule whilst the alkyl chain is the hydrophobic region.

The structural analysis of 1:1 crystal complex of 10TAC/BNP reveals a triclinic lattice with $\overline{P1}$ symmetry, *formula* $C_{33}H_{42}NClO_3$, *formula weight* 536.15, *crystal size* $0.10 \times 0.20 \times 0.10\,mm^3$, $a = 9.999(1)$ Å, $b = 19.420(1)$ Å, $c = 8.977(9)$ Å, $\alpha = 92.845(8)^\circ$, $\beta = 112.718(7)^\circ$, $\gamma = 98.396(7)^\circ$, $V = 1579.9(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.135\ g\,cm^{-3}$, $m.p = 168.7^\circ C$.

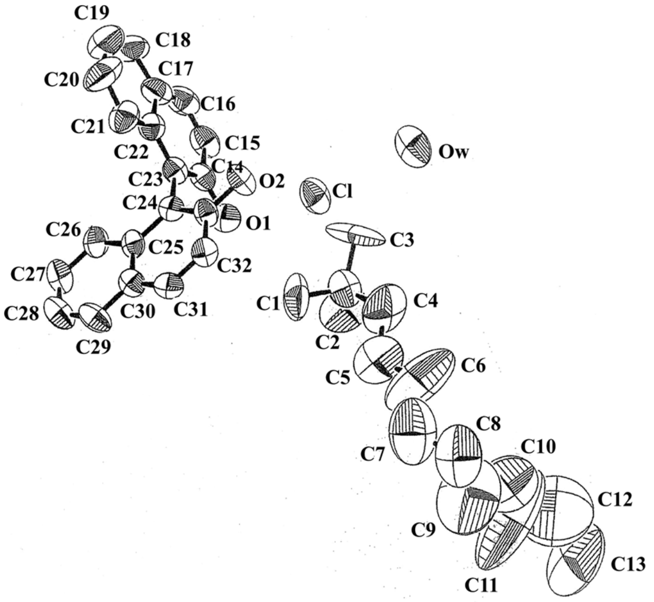

FIGURE 2 The molecular structure and atomic numbering of 1:1 complex of 10TAC/BNP. The 40% probability ellipsoids are shown. Hydrogen atoms omitted for clarity.

In respect to the molecular geometry of 10TAC/BNP complex, there are no significant differences in bond lengths and angles observable in the crystal complex. The observed bond lengths and angles are normal and lie within the range of values usually observed in monoalkyltrimethylammonium halide molecules or with its complexes involving planar organic molecules [7–10]. The bond angles and lengths lie in the range from 1.505(5) to 1.530(2) Å for C-C and from 111(2) to 112.8(6)° for C-C-C and from 1.520(5) to 1.551(5) Å for N-C and from 108.2(4) to 111.1(4)° for C-N-C. The average bond lengths and angles are: 1.520(5) Å for C-C bond, 112.0(6)° for the C-C-C angle, 1.533(5) for the N-C bond, and 109.4(4)° for C-N-C angle. The average values are also not significantly different from those usually observed in monoalkyltrimethyl ammonium halides [11]. The C-C-C-C torsion angles are in the range of $180 \pm 41°$ with the exceptions of C6-C7-C8-C9 (−59(3)°) and C7-C8-C9-C10 (75(3)°) and suggest two *gauche* conformations about C7-C8 and C8-C9.

In the naphthol moieties, the bond lengths and angles are in the range from 1.34(1) to 1.44(2) for C-C and from 117(1) to 123.8(9)° for C-C-C, 1.342(9) to 1.35(1) Å for O-C bond and 118.6(6) to 120.7(6) for O-C-C angle. The C-C bond joining the two naphthol groups is in length of 1.48(1) Å, which corresponds to that observed in the *cisoid* racemate conformation (1.475 Å) [12]. The O-C bond lengths are also in conformity with the corresponding values observed in binaphthyl systems [13] and close to the usual value for C-O bond length (1.36(2) Å) in phenols [14]. The dihedral angle between the two naphthol planes defined by O1, C14,…,C23 and O2, C33,…,C24 in BNP is 85.1(1)°. The OH groups in the BNP molecule also adopt the *cis* mode. The mean deviation from the planarities of these naphthol moieties are 0.0231(1) and 0.0092(2)Å.

As a general result of these data on the host and guest molecules, it is obvious that the molecular geometry of the host and guest are not significantly influenced by the formation of crystal complex.

3.3. Crystal Packing in 10TAC/BNP Complex

The crystal structure of 10TAC/BNP viewed along the *a*-axis is shown in Fig. 3. The unit cell consists of two BNP molecules and two 10TAC molecules. In the unit cell, the naphthol planes of the BNP molecule are completely trapped between the alkyl chains of 10TAC molecules in an arrangement where two aligned naphthol planes run between two alkyl chains in opposite directions. The OH groups of the naphthol moieties are directed towards the polar region comprising of the hydrophilic head part of 10TAC and water molecules, whilst the

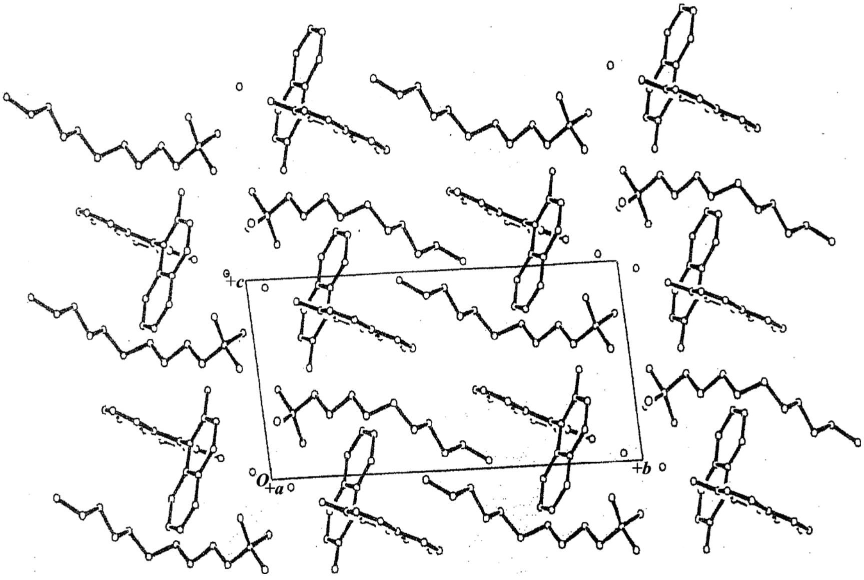

FIGURE 3 Crystal structure of 10TAC/BNP viewed along the *a*-axis.

hydrophobic part of BNP molecule pack in the hydrophobic region involving the tail region of the alkyl chains. The packing structure of 10TAC/BNP shows a distinct similarity in the packing structure observed in those observed in crystal complexes of monoalkyltrimethylammonium halides with planar aromatic molecules as shown in a schematic diagram (Fig. 4).

For the description of the crystal structure, intermolecular contacts within the sum of the van der *Waals* radii suggested by Bondi [15] for the pair of interacting atoms have been used. The combined actions of hydrogen bonding, electrostatic interactions and C-H$\ldots\pi$ interactions contribute significantly to the stability and formation of the crystal complex. The host-guest molecules are held together by hydrogen bonds viz; Cl$\cdots$O2 3.033(5) Å, Cl$\cdots$Ow 3.060(8) Å (Fig. 5). The hydrogen bond network (Fig. 5) is favorable to keep the naphthol planes in an arrangement (L-shaped) to align both the naphthol planes and the alkyl chains parallel to each other in a fashion that enhances complete inclusion of the guest between host molecules as usually observed in complexes between monoalkyltrimethylammonium halides with planar aromatic molecules. This suggests that the arrangement of the naphthol planes as per controlled by the hydrogen bond network plays significant role in the packing structure. The arrangement of the

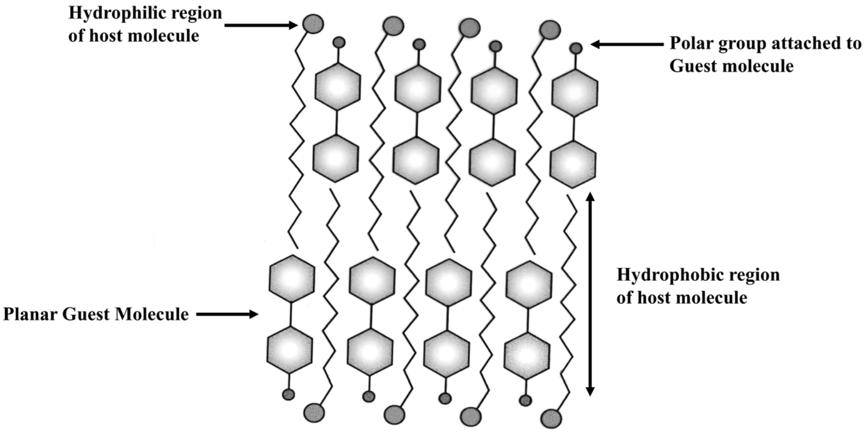

FIGURE 4 Schematic diagram of a packing arrangement of monoalkyltrimethyl ammonium halides with the planar aromatic molecules.

naphthol planes which are almost normal to each other is evident in the dihedral angle between the two naphthol planes defined by O1, C14,…,C23 and O2, C33,…,C24 in BNP is 85.1(1)°).

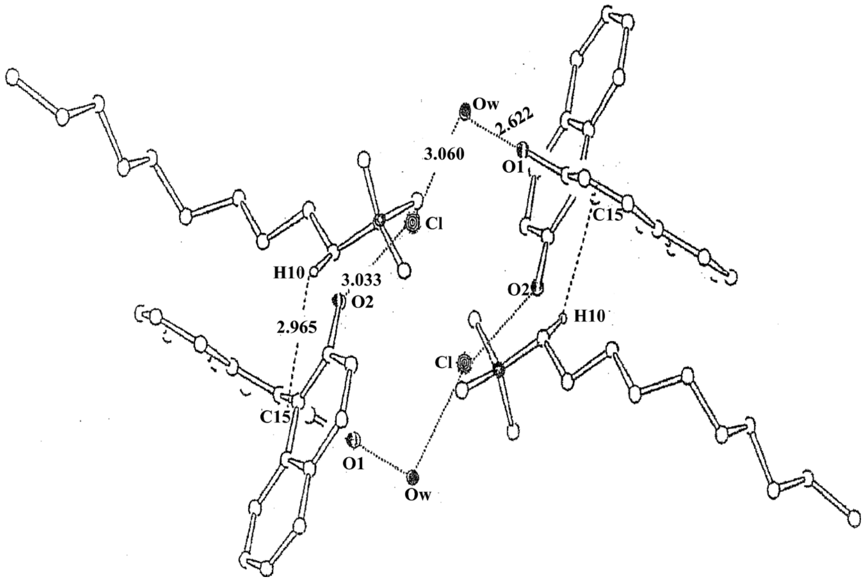

FIGURE 5 Hydrogen bond interactions in the 10TAC/BNP (viewed along a-axis). The broken lines represent C-H$\cdots\pi$ interactions, whilst the dotted lines represent hydrogen bonds.

The electrostatic interactions occur between the chloride anion and nitrogen cation, and the shortest distance of $Cl^{-}\cdots N^{+}$ being 4.48 Å, whilst the C-H$\cdots\pi$ interaction (Fig. 5) exists between the C-H of an alkyl chain and carbon atom of a naphthol moiety. The short C-H$\cdots$C distance which is suggestive of observed C-H$\cdots\pi$ interactions was C15$\cdots$C10 2.96 Å. The short contacts between non-bonded carbon atoms with values less than that of the sum of van der Waals (3.54 Å) [15] are C1$\cdots$C32 3.34(1), C2$\cdots$C25 3.39(1), C2$\cdots$C29 3.52(1), and C2$\cdots$C30 3.34(2) Å. The shortest guest–guest intermolecular distance was 3.94 Å, whilst that of host–host shortest intermolecular distance was 4.20 Å, and thus suggests that the packing of the 10TAC molecules are dependent on the packing of the BNP molecules.

CONCLUSIONS

The pattern or network of hydrogen bond interactions has significant influence to manipulate the kind of molecular packing fashion of host and guest molecules in a crystal complex. In the 10TAC/BNP complex, the packing patterns of the guest (BNP) molecules between host molecules (10TAC) suggest that the arrangement of the naphthol planes (which are almost normal to each other) as well as that of the alkyl chains as per controlled by the hydrogen bonding network was favorable for the complete entrapment of BNP molecules between 10TAC molecules. The formation of the 10TAC/BNP complex can be obtained by crystallization from solution as well as by the method of mixing powdered samples in a mortar.

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